

CATALYTIC HYDROLIQUEFACTION OF COALS FOR HYDROCARBON-TYPE ANALYSIS IN RELATION TO REFINING

by

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INTRODUCTION

Small samples of liquids have been prepared from several coals of widely varied rank by catalytic hydrogenation in a batch autoclave. The liquids were prepared at conditions designed to minimize cracking of hydrocarbon components, yet were upgraded to remove nitrogen and to permit detailed determination of hydrocarbon types potentially obtainable for refining. This paper covers the preparation and properties of the liquids; the hydrocarbon analyses will be reported later.

Scattered literature references indicate that the complexity of hydrocarbon groups in coals and in liquefaction products varies substantially with the rank or grade of coal liquefied. Reports of early German technology refer repeatedly to the liquefaction of brown coal (lignite) at about half the hydrogenation pressure required for bituminous coals (9). The asphaltene content of recycled oil in continuous hydrogenation of German coals decreased with decreasing grade of coal and reached an apparent minimum in the range of sub-bituminous coals. Although there were gaps in the data, this trend, combined with greater rates of hydrogenation observed for the product oils, indicated smaller polynuclear hydrocarbon units as well as different chemical structure in brown coals in comparison with bituminous coals. The greater reactivity was also associated with increased oxygen content. Wender (8) suggested that hydrocarbon groups in coal can vary from those which contain little more than one aromatic ring, as in lignite, to virtually one huge fused-ring aromatic in anthracite coal. However, most coal liquefaction research in this country has been done on bituminous coals. U.S. Bureau of Mines work in the 1940 era recognized the greater reactivity of lower-rank coals and the importance of catalysts in promoting formation of hydroaromatic compounds that function as hydrogen donors in liquefaction (6). In fact, low-rank coals were so reactive that high hydrogen pressure was required to avoid repolymerization of reactive fragments to coke at the temperatures used, generally about 430° C. However, almost complete liquefaction and extensive oxygen removal could be obtained at relatively low temperature and with relatively little hydrogen consumption (but with hydrogen transfer from solvent). The rate of conversion of Pittsburgh bituminous-A coal to asphaltenes was considerably greater than conversion of the asphaltenes to oil, while the opposite was true for coal of bituminous-C rank from Rock Springs, WY (9). The wt-pct yield of total oil increased with rank of coal from about 55 for lignite to 65 for sub-bituminous to 70-75 for high-volatile bituminous coal on a moisture- and ash-free (maf) basis. Yields were much less for still higher-rank medium-volatile coals because of low reactivity. These trends were observed in both batch autoclave and continuous-flow units with stannous sulfide catalyst. Characterization of the liquid products was limited to distillate fractions, usually a small part of the product, which were determined to be highly cyclic and aromatic. Phenolics content was greater in distillates from coal of lower rank.

Among more recent studies, the effluent from liquefaction of a Utah sub-bituminous coal with hydrogen donor solvent (3) contained less benzene insoluble material than that from Pittsburgh bituminous coal, and addition of a paraffinic diluent was required to precipitate enough asphaltenes for agglomeration of residual solid particles. Other sub-bituminous coal products behaved similarly. In reports of the HRI, Inc., H-Coal process (7) and the Gulf Science and Technology Co. CCL (catalytic coal liquefaction) process (4), syncrudes produced from sub-bituminous coals contained less heavy ends and less polynuclear aromatics with 4 or more rings. An extensive survey of coals

with respect to liquefaction by hydrogenation (1) confirmed early reports that high volatile bituminous coals gave the best yields, but the products were not characterized in any detail.

EXPERIMENTAL

Materials

Table 1 shows analyses of the coal samples used. The analyses were run by the U.S. Bureau of Mines, Pittsburgh, PA. The lignite was supplied by the Grand Forks, ND, Energy Research Center, the Wyodak coal by Hydrocarbon Research, Inc., Trenton, NJ, and the other four samples by Conoco Coal Development Co., Library, PA. Those samples not already pulverized were ground and screened to -50 mesh. The lignite and Wyodak coal samples were dried under vacuum and kept under nitrogen thereafter. The others were used as received. Note that the nitrogen content of the bituminous coals was about 50 percent greater than that of the sub-bituminous coals and lignite. Indicated oxygen content of the dry coals increased from about 8 to 19 wt pct as the rank or grade decreased. The W. Kentucky coal had a high sulfur content of 4.3 wt pct.

TABLE 1. - Analyses of Coals

Source	PA-WV	Illinois	W. KY	Montana	Wyoming	N. Dakota
Seam	Pittsburgh	No. 6	--	(Colstrip)	(Wyodak)	Beulah Std. II
Rank	hvb A	hvb B or C	hvb B or C	sub-bit. A	sub-bit. C	Lignite
Proximate analysis (as received)						
Moisture	1.7	7.8	2.9	4.2	10.9	28.0
Volatile matter	35.9	34.2	38.4	34.4	39.5	31.0
Fixed carbon	55.1	51.4	48.8	48.5	42.7	33.3
Ash	7.3	6.6	9.9	12.9	6.9	7.7
Ultimate analysis (moisture free)						
Hydrogen	5.1	4.9	4.9	4.3	4.8	4.5
Carbon	76.9	75.2	70.2	65.2	66.8	63.5
Nitrogen	1.5	1.6	1.4	0.6	1.0	0.9
Sulfur	1.6	1.5	4.3	1.8	0.5	1.3
Oxygen (difference)	7.6	9.7	8.8	14.5	19.2	19.1
Ash	7.4	7.1	10.2	13.5	7.8	10.7

Nickel-molybdenum/alumina hydrotreating catalyst, American Cyanamid HDS-3A, was crushed, screened to 60-100 mesh, and dried overnight at 200° C. Elemental sulfur was added in liquefaction runs to provide some sulfiding of the catalyst. For upgrading the crude liquids, the catalyst was presulfided in the autoclave as a slurry in n-octane plus carbon disulfide, 400 psig added hydrogen, and at 285° C maximum temperature. The diluent was flashed off at 225° C to insure elimination of water.

The initial solvent for each preparation was 99 percent tetralin from the Aldrich Chemical Co.

Procedure

Both liquefaction and upgrading runs were made in a 2-liter MagneDrive autoclave from Autoclave Engineers, Inc. A typical liquefaction charge was 325 - 400 g coal, 500 g solvent, 50 g catalyst, and 4 g sulfur. The charged reactor was purged with nitrogen and hydrogen, pressured with hydrogen to about 1,500 psig, leak tested, and heated to 300° C in about one hour. The temperature was then raised slowly over a period of several hours, depending upon the rate and extent of hydrogen consumption, to a maximum of 400° C. Cylinder hydrogen was boosted to about 3,300 psig with a Whitey compressor, and it was added periodically to the reactor from a calibrated surge volume to maintain reactor pressure between about 2,450 and 2,700 psig. At the end of a run the reactor was cooled rapidly to 260° C, and nearly all the gaseous components were bled off to remove water and some light ends. The effluent gas passed through a condenser and ice-cooled trap, a scrubber column filled with 1/4-inch screen saddle-type packing, and a second ice-cooled trap, after which it was sampled and metered. The top section of the packed column was heated to break the fog which passed the first trap. The product slurry, cooled to about 70° C, was removed from the reactor by suction through a dip tube and was filtered through Whatman No. 41 paper in a heated Buchner funnel, at 50 - 60° C. Filtered liquid product was used as diluent for the following run. The filter cake was washed with benzene at 50° C and dried to determine residual solids. Runs were repeated until the calculated tetralin content of the recycled liquid was less than 6 wt pct, and then were continued to accumulate at least 1,200 g of crude liquid (including benzene washings and light ends). The reactor was flushed with hot benzene only at the end of a series, since complete recovery from single runs was not essential. The reactor was opened occasionally to inspect for accumulated deposits, which generally were insignificant.

The crude liquids were upgraded in similar autoclave runs to remove heteroatoms, especially nitrogen. A typical charge was 100 g presulfided catalyst and 850 g crude liquid.

Effluent gases were analyzed by gas chromatography. Hydrogen consumption was taken as the difference between that charged and withdrawn. No attempt was made to account for sulfur, nitrogen, or oxygen, although water recovery was nearly quantitative in later runs. Overall material balances were calculated, recognizing the limitations of the procedures used, but the objective was to obtain liquids which contained most of the hydrocarbons potentially obtainable from the coal, not to provide quantitative process data.

The upgraded liquids were vacuum distilled in a Perkin-Elmer spinning band column to an overhead temperature of 425° C, corrected to atmospheric pressure. Asphaltenes were removed from the > 425° C residuum by pentane precipitation (5), and the asphaltene-free residuum was then vacuum flashed at 540° C, corrected to atmospheric pressure.

RESULTS

The results of the liquefaction experiments are summarized in Table 2. The data for each coal are a composite of those for successive batches from which product liquid was retained. Total products accounted for varied from 90 to 105 wt pct of coal charged. The variations reflected mostly uncertainty in reactor holdup at the start of product accumulation, incomplete recovery of water and possibly removal of sulfur from W. Kentucky coal. Net yields of liquid varied from 69 wt pct from Illinois coal to 55 wt pct from lignite. The yields of C₁ - C₄ light gases decreased and that of CO₂ increased as the rank of coal decreased. Hydrogen consumption increased by about 15 percent as the rank of coal decreased, with the exception of Pittsburgh coal to be noted later. The reaction times briefly summarized in Table 2 show that the major part of the reaction was at temperatures less than 375° C, except for Pittsburgh coal, and that less total time was required to yield a readily filterable product slurry from the lower-rank coals.

TABLE 2. - Batch Liquefaction of Coals
2,450-2,800 psig, NiMo Catalyst

Coal	Pittsburgh	Ill. No. 6	W. Ky.	Colstrip	Wyodak	Lignite
Wt-pct of coal charge:						
Net liquid	66	69	62	58	60	55
Gas: C ₁ - C ₄	5.8	5.0	5.2	3.2	4.2	4.2
C ₅ +	2.8	0.9	1.0	1.3	2.2	2.2
CO ₂	0.1	0.5	0.7	3.2	5.6	5.6
Residual solids	19	19	18	32	21	20
Total products	101	97	90	104	106	102
H ₂ consumed	4.3	4.0	4.0	4.4	4.8	4.6
Reaction time, hrs. at °C:						
325 - 375	5.2	7.6	10.3	6.8	6.8	5.6
376 - 400	5.2	2.6	2.0	2.1	1.9	1.6
Total	10.4	10.2	12.3	8.9	8.7	7.2

Most of the hydrogen consumption also occurred at less than 375° C, again with the exception of Pittsburgh coal.

Averaged temperature-time curves for the liquefaction reactions are shown in Figure 1. Temperatures were increased as needed to maintain a suitable rate of hydrogen consumption. The maximum temperature was set at 400° C to minimize hydrocarbon cracking, except for an initial preparation from Illinois coal for which data are not included. Temperatures up to 415° C were used in that series, and yields of methane increased significantly. The bituminous coals showed no substantial consumption of hydrogen, as indicated by pressure decrease, at less than about 350° C. Pittsburgh coal was the least reactive, with the indicated rate of hydrogen consumption being about half that of the other bituminous coals and one-third that of the lower-rank coals. To overcome this, maximum reactor pressure for Pittsburgh coal was increased to 2,800 psig. Coupled with less production of water, this resulted in sharply increased partial pressure of hydrogen in the reactor. Reaction rates actually increased as the series progressed, in contrast to behavior of the other coals. This improved rate was attributed to the formation of hydroaromatics of higher molecular weight which were better hydrogen donor solvents than the tetralin used as starting solvent. Hydrogen consumption by the sub-bituminous coals and lignite began at 325° C or less, as reflected in the curves of Figure 1, and most of the hydrogen was consumed at less than 350° C. In fact, too rapid an increase in reaction temperature for these coals resulted in an overall decrease in hydrogen consumption and a viscous product which was difficult to handle. Reaction temperature was still programmed to 400° C, however, for increased heteroatom removal from the liquid and resultant molecular weight decrease.

The results of upgrading the crude coal liquids by similar batch hydrogenations with pre-sulfided catalyst are summarized in Table 3. Results for the Wyodak coal were not complete when the manuscript was submitted. The objective was to decrease nitrogen content of the liquids to 0.2 to 0.3 wt pct with a minimum of cracking of hydrocarbons. The ratio of oil to catalyst in the autoclave was far greater than in a typical trickle-flow operation over fixed-bed catalyst, by a factor of up to 50-fold. Thus, longer reaction time was required, and

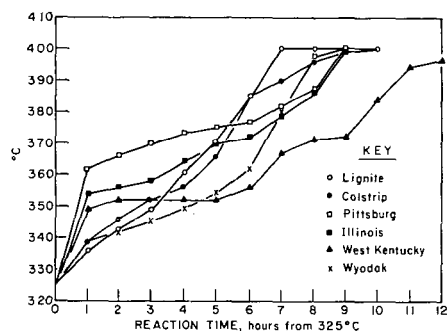


FIGURE 1 LIQUEFACTION OF COALS

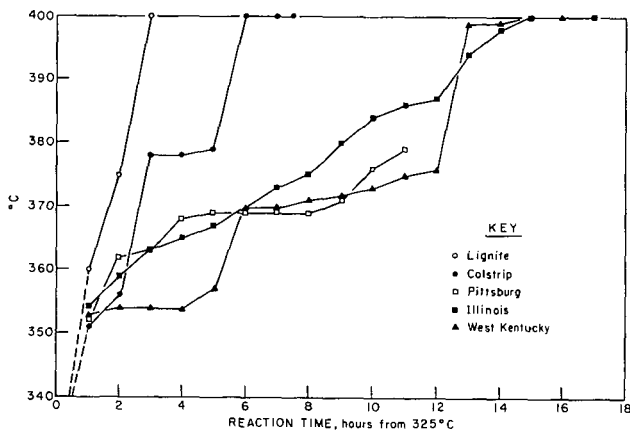


FIGURE 2 UPGRADEING OF COAL LIQUIDS

TABLE 3. - Upgrading Coal Liquids
2,450 - 2,650 psig, NiMo Catalyst (Presulfided)

Coal	Pittsburgh	Ill. No. 6	W. Ky.	Colstrip	Lignite
Wt-pct of charge:					
Liquid product	92	92	92	93	95
Gas: C ₁ - C ₄	0.3	1.8	2.0	0.8	0.3
C ₅ +	1.0	0.8	0.8	0.2	0.9
Total products	95	97	97	97	98
H ₂ consumed	1.0	2.3	2.3	1.6	0.9
Reaction time, hrs. at °C:					
325 - 375	9.8	8.7	12.7	4.7	2.0
376 - 400	<u>0.9</u>	<u>9.3</u>	<u>6.4</u>	<u>2.9</u>	<u>0.7</u>
Total	10.7	18.0	19.1	7.6	2.7

increased temperature could not be substituted for time without increased cracking of hydrocarbons originally present. The liquids from Illinois and W. Kentucky coals required up to 19 hours reaction time; however, even in those runs over 60 percent of the hydrogen was consumed at less than 375° C. Much shorter reaction times were required for upgrading the liquids from lower-rank coals and lignite. Recovery of upgraded liquid was 92 to 95 wt pct of the charge, not including C₅ + material in the effluent gas. Hydrogen consumptions and yields of gaseous hydrocarbons were small, except for the two liquids which required extended reaction. Temperature-time curves for the upgrading are shown in Figure 2. No appreciable hydrogenation occurred at less than 350° C, and reactions of all except the Pittsburgh liquid were programmed to 400° C. The Pittsburgh run was cut short when that liquid was found to have been substantially upgraded during the liquefaction as previously noted.

Properties and some elemental analyses of the crude and upgraded liquids are given in Table 4. Nitrogen content of the crude liquids from bituminous coals was 1.1 to 1.3 wt pct, compared to 0.4 to 0.6 wt pct in those from lower-rank coals. The exception, again, was that from Pittsburgh coal, for which more hydrogenation during liquefaction had decreased nitrogen content to 0.4 wt pct. Oxygen content in several of the crude liquids, determined by neutron activation analysis, was 1.3 to 2.1 wt pct. Nitrogen content of all the upgraded liquids was decreased to about the same level, in the range of 0.2 to 0.3 wt pct. Sulfur content was, of course, small in all cases. The upgraded liquid from Pittsburgh coal was the most viscous, but differences were small since the extent of upgrading was controlled to bring all liquids to the same nitrogen content. Pour points of the upgraded liquids varied from less than 5° F for liquids from bituminous coals to +45° F for that from lignite, reflecting increased paraffin content in the latter. However, a few percent of waxy n-paraffins can increase pour point sharply.

Distributions of the upgraded liquids by distillation and asphaltene content are shown in Table 5. Asphaltene contents were in the range of 4.7 to 6.8 wt pct and, thus, correlated well with nitrogen contents to indicate that all liquids had been brought to a similar level of upgrading to a predominantly hydrocarbon product. The distribution by boiling range was similar for all the liquids. This may be surprising in view of the greater reactivity of the lower-rank coals, but relatively little upgrading of the crude liquid was required in those cases.

TABLE 4. - Properties of Crude and Upgraded Coal Liquids

Coal	Pittsburgh	Ill. No. 6	W. Ky.	Colstrip	Lignite
Crude liquid:					
Nitrogen, wt-pct	0.44	1.10	1.28	0.64	0.43
Oxygen, wt-pct	-	1.34	2.09	1.61	-
Upgraded liquid:					
Specific gravity, 60/60° F	0.99	0.99	0.99	0.99	0.98
SSU vis. @ 100° F	441	126	89	263	181
Pour point, ° F	+5	<5	<5	+20	+45
Carbon, wt-pct	89.2	88.6	88.2	88.1	89.0
Hydrogen, wt-pct	10.8	10.3	10.7	10.6	10.8
Sulfur, wt-pct	<.01	.02	.02	<.01	<.01
Nitrogen, wt-pct	.20	.25	.29	.19	.25
Oxygen, wt-pct	-	.19	.32	.32	-

TABLE 5. - Distribution of Upgraded Coal Liquids

Coal	Pittsburgh	Ill. No. 6	W. Ky.	Colstrip	Lignite
Distillation, wt-pct					
<200° C	10.0	11.4	16.6	11.5	12.3
200 - 325° C	21.7	27.9	26.1	21.5	24.0
325 - 425° C	20.3	22.5	22.8	21.1	20.7
425 - 540° C*	26.6	23.7	19.7	21.0	21.0
>540° C*	16.2	7.5	9.3	18.3	15.0
Asphaltenes	4.7	6.8	5.2	6.6	6.7

*Asphaltenes removed from > 425° C resid.

Table 6 gives the specific gravities and nitrogen contents of the distillation fractions. The trends are as expected, with nitrogen concentration greatest in the residuum.

DISCUSSION

The results reported here indicate that a wide variety of coals can be liquefied by catalytic hydrogenation at conditions which permit recovery of most of the hydrocarbons potentially obtainable from a given coal. By control of the extent of upgrading of the crude product, liquids of which about 90 percent can be analyzed for hydrocarbon type have been prepared. Such analyses will provide information on the effect of coal source on the character of potential feedstocks for production of refined fuels. Differences in the required extent of upgrading of the crude liquids may have decreased the spread in complexity of hydrocarbon types recovered, but in view of the relatively low reaction temperatures used and the small yields of gaseous hydrocarbons, not much

TABLE 6. - Distillation Fractions of Upgraded Liquids

Coal	Pittsburgh	Ill. No. 6	W. Ky.	Colstrip	Lignite
<200° C distillate:					
Specific gravity	0.829	0.827	0.832	0.822	0.822
Nitrogen, wt-pct	.003	.001	.096	.023	.007
200 - 325° C distillate:					
Specific gravity	.915	.926	.919	.918	.916
Nitrogen, wt-pct	.016	.021	.062	.030	.104
325 - 425° C distillate:					
Specific gravity	.983	1.001	.993	.982	.983
Nitrogen, wt-pct	.076	.159	.200	.119	.304
425 - 540° C distillate:*					
Specific gravity	1.045	1.061	1.049	1.032	1.032
Nitrogen, wt-pct	.272	0.415	0.415	0.233	0.412
>425° C resid.					
Sulfur, wt-pct	<.01	<.01	.04	.02	<.01
Nitrogen, wt-pct	.37	.56	.57	.33	.50
Asphaltenes, wt-pct	9.9	17.9	15.3	14.3	15.7

*Asphaltenes removed

cracking of heavier hydrocarbons should have occurred. The reaction conditions used for lignite, for example, could not have been applied to Illinois coal to recover any substantial part of the hydrocarbons for analysis. On the other hand, a crude liquid from one of the low-rank coals could be upgraded on the same temperature-time program as was used for Illinois coal, and this is planned.

The upgraded coal liquids described in this paper are being analyzed in detail for hydrocarbon-type composition by methods developed for petroleum and adapted to the analysis of synthetic crude oils (2). The results will be reported later when completed.

ACKNOWLEDGEMENT

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STANNOUS CHLORIDE AND COBALT MOLYBDATE-ALUMINA CATALYSTS
IN HYDROGENOLYSIS OF SOLVENT REFINED COAL

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Abstract

The relative effectiveness of SnCl_2 and $\text{Co/Mo/Al}_2\text{O}_3$ (silica-stabilized) for the hydrogenolysis of solvent-refined coal was studied in a batch autoclave with tetralin as solvent. SnCl_2 was exceptional in higher H_2 consumption, higher liquefaction, and higher ratio of low molecular weight products in the oil fraction than either $\text{Co/Mo/Al}_2\text{O}_3$ or in catalyst-free tests. Discrimination between catalysts with respect to S elimination was difficult because of the low S content of SRC; however, the effectiveness with respect to both N and O elimination decreased in the order $\text{SnCl}_2 > \text{No Catalyst} > \text{Co/Mo/Al}_2\text{O}_3$. Oil production was also lower with $\text{Co/Mo/Al}_2\text{O}_3$ than with no catalyst, an effect which may be due to the SiO_2 present as a stabilizer in the support Al_2O_3 . The results are consistent with the concept that coal ash catalyzes the difficult step of converting asphaltene to oil.

Introduction

One of the intriguing aspects of catalytic coal liquefaction-hydrodesulfurization is that multifunctional catalysts are desirable, as is also true in the well-known cases of naphtha reforming and of hydrocracking in petroleum refining. Most of the individual catalysts best studied in coal processing are at least bifunctional, although this aspect has not received much explicit attention. The role of SnCl_2 (or $\text{Sn} + \text{HCl}$, or $\text{Sn} + \text{NH}_4\text{Cl}$) in coal liquefaction is still not understood after some decades of study, but clearly the catalyst exercises cracking as well as hydrogenative functions. The catalysts consisting of "cobalt molybdate" supported on silica-stabilized alumina are acidic, whatever their detailed action may be in the hydrodesulfurization of coal or coal-derived liquids.

It is an interesting fact that the best catalyst for liquefaction of coal is not best for hydrodesulfurization. The comprehensive catalyst survey of Kawa et al. (1974) provides a recent illustration. Supported SnCl_2 , even in small concentration, was outstanding in its ability to promote both total liquefaction and the production of benzene-soluble oil, but not in desulfurization. Supported "cobalt molybdate" was equally outstanding in giving products of low S content, but not in liquefaction.

The study of catalysts for coal hydrogenolysis is essential, but the catalytic effects of coal ash itself may confound the interpretation of the effects of added catalysts. There is some advantage, therefore, in studying

added catalysts for the hydrogenolysis of solvent-refined coal (SRC) rather than of coal itself. SRC is essentially ash-free.

The present limited study was intended to explore what seem to be extreme cases of catalytic action, with the use of SRC as feed. The study is a comparison of (a) no catalyst, (b) unsupported SnCl_4 at low concentration, and (c) a commercial $\text{Co/Mo/SiO}_2\text{-Al}_2\text{O}_3$ at low concentration. In some ways SRC is a reasonable "model compound" with which to study the difficult steps in coal-to-oil conversion free of the complication of intrinsic catalyst (ash). The sample of SRC was almost completely soluble in pyridine, in Soxhlet extraction; only 17% soluble in either benzene or toluene; and almost insoluble in n-pentane (< 2%). The difficult steps of converting pyridine-solubles to "asphaltene" and "oil", as well as of hydrodesulfurization, may therefore be followed conveniently with SRC as feed.

Experimental

Equipment

All autoclave experiments were conducted with the same 1-l. stirred autoclave (Autoclave Engineers Model MB-1005 Magnedash) used in the work of Yen et al. (1976). As in the earlier studies, a glass liner was used in the autoclave to eliminate possible catalyst "memory effects". The following changes were made in equipment used for product analyses:

1. At the conclusion of a run, after cooldown, autoclave gas was passed through 2N zinc acetate solution (rather than caustic) in the scrubbing bottles, to remove H_2S and permit subsequent analysis of H_2S by an iodometric method.
2. After the scrubbing bottles, the autoclave gas was passed through an on-line gas chromatograph (Perkin-Elmer Model 810) for analysis of light hydrocarbons. The column was 7 ft. x 1/8 inch Porapak Q, operated at 80°C.; flow rate of the He carrier was 45 ml./min.
3. Analysis of the "oil" samples was performed with a Varian Aerograph gas chromatograph, Model 1420, equipped with 5 ft. x 1/8 inch columns packed with 1.5% OV-101 on 100/120 Chromosorb G-H.P., with a helium carrier flow rate of 25 ml./min. The column was operated isothermally at 125°C. for the first 3 minutes after sample injection, after which the column temperature was increased from 125°C. to (a maximum of) 270°C. at the programmed rate of 15°C./min. The G.C. data were processed with a Varian CDS-111 Data System and visually displayed on a Leeds and Northrup Azar recorder.

Materials

The solvent-refined coal used in this work was obtained, through the courtesy of Mr. E.L. Hoffman, from the pilot plant operated in Wilsonville, Alabama by Southern Services, Inc. Our material, said to have been made from

Kentucky No. 14 coal, has the following elemental analysis: 86.77% C, 6.0% H, 1.3% N, 0.7% S, and 5.3% O (by difference). These values are close to, but differ slightly from, "typical values" reported for the Wilsonville plant. Ash was about 0.2%.

The tin chloride used as catalyst was ACS grade $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, obtained from Fisher Scientific Co. The $\text{Co/Mo/Al}_2\text{O}_3$ catalyst was Harshaw Type 0402T, containing approximately 15 wt.% MoO_3 and 3 wt.% CoO on silica-stabilized alumina (5% SiO_2). Its properties are given in greater detail in Yen et al. (1976).

Procedures

Procedures for the autoclave experiments were essentially the same as those used by Yen et al. (1976), except for the addition of a solid-state temperature controller (Barber-Colman Model 520) for the 2 kw. furnace. Internal temperatures were monitored by a chromel-alumel couple, inserted in the autoclave thermowell, connected to a millivolt potentiometer. Initial (cold) H_2 pressure was 1000 psig in all experiments. The autoclave "dasher" was operated during heatup and the reaction period of 1 hr. at 450°C . ($\pm 5^\circ\text{C}$.) at the constant frequency of 180 strokes per minute.

The procedures for analyzing the letdown gases at the conclusion of a run have been described above. A series of eight gas samples was taken during the letdown period for G.C. analysis; the analyses for any single run were integrated to obtain total gas composition.

After the autoclave was unsealed, the glass liner with its contents was removed for analysis. Some material, found outside the liner in the bottom of the autoclave, was removed by aspiration, collected, and weighed; it was denoted as "autoclave residue". Although the average amount of "autoclave residue" was approximately 14 wt.% of the total initial charge (75g. SRC + 300g. tetralin), it was not included in the mass balance or in the product separation scheme because of possible catalytic effects of the metal autoclave walls.

The separation scheme used for liquid and solid products is summarized in Figure 1. Distillations in Run 1 (see Table I) were performed at atmospheric pressure, as was done by Furlani et al. (1976). In all other runs, the distillations were generally conducted at 30-35 Torr. under a N_2 atmosphere. Separation of "asphaltols" (toluene-insoluble, pyridine-soluble material) was effected in only a few runs; the results are therefore not included in this paper. Occasionally naphthalene was observed to be condensing during the tetralin distillation. When this occurred, the vacuum distillation was carried to a vapor temperature somewhat in excess of 105°C ., cooling water was drained from the condenser, and a heat gun was employed to drive the naphthalene into the tetralin distillate. The pot temperature was always kept below 250°C . in this distillation. Further details of the separation scheme are to be found in Lovetro (1977).

Analyses for C, H, and N were performed with a Perkin-Elmer Model 240 Analyzer in the Department of Chemistry of this university. Analyses for S were very kindly provided through the courtesy of the Hooker Chemical Co.

Results and Discussion

The catalysts used in the various autoclave runs are summarized in Table I. Also shown are the weights of H_2 consumed in each run, calculated by difference, and the weights of H_2S absorbed in the zinc acetate scrubbers.

Table I

Autoclave Tests: H_2 Consumed and H_2S Discharged*

Run No.	Catalyst	Hydrogen (g.)			H_2S Discharged (g.)
		Charged	Discharged	Consumed**	
1	None	3.56	2.43	1.13	0.0154
1A	None	4.44	3.42	1.02	0.0528
2	$SnCl_2$ ***	4.45	Not detnd.	Not detnd.	0.0139
2A	$SnCl_2$	4.53	2.78	1.75	0.0219
2B	$SnCl_2$	4.53	2.71	1.82	0.0416
3	$Co/Mo/Al_2O_3$ ****	4.43	3.43	1.00	0.0487
3A	$Co/Mo/Al_2O_3$	4.49	3.31	1.18	0.0416

*75g. SRC + 300g. tetralin charged to glass liner.

** H_2 consumption by difference.

***1g. $SnCl_2 \cdot 2H_2O$ charged.

****1g. Harshaw 0402T ($Co/Mo/SiO_2-Al_2O_3$) charged as 40-60 mesh particles.

There was considerable scatter in the H_2S data. However, the S measured as H_2S was in all cases less than 10% of that charged in the 75g. of SRC. Substantially more elimination of S actually occurred, based on the analyses of asphaltene and oil shown in Table II. Sulfur analyses of the toluene and tetralin distillates show the presence of small amounts of low-boiling sulfur compounds, and the "missing" S is probably to be accounted for in these cuts.

Of particular interest is the H_2 consumption in the run with $SnCl_2$ catalyst (Series 2). It was much higher than in the blank runs (Series 1) or in the runs with $Co/Mo/Al_2O_3$ (Series 3). This result may be correlated with the relatively poor material balances in the $SnCl_2$ runs (cf. Table IV, below) and with the relatively rich content of low-boiling constituents in the "oil" fraction from the $SnCl_2$ runs (cf. Figure 2, below).

The difference between average values for H_2S discharged, for the blank runs and for those with $SnCl_2$ or $Co/Mo/Al_2O_3$, was found by application of the "t" test to be significant only at the 80% level. Values for the weight of CH_4 discharged are not shown in Table I. These showed almost no variation, run to run, and the average value for CH_4 produced was about 1.7g. This corresponds to a conversion to CH_4 of about 2% of the carbon in the 75g. of SRC charged.

Table II contains the elemental analyses for the oil and asphaltene fractions from each run.

Table II
Elemental Analyses

Run No.	Product	Atom Ratio (H/C)	Wt.% C	Wt.% H	Wt.% N	Wt.% S	Wt.% O (by dif.)
Feed	--	0.83	86.66	5.99	1.33	0.70	5.32
SRC							
1	Oil	1.20	87.57	8.74	0.05	0.09	3.55
	Asphaltene	0.77	89.62	5.77	1.82	0.38	2.41
1A	Oil	1.11	88.32	8.20	0.24	0.27	2.97
	Asphaltene	0.87	88.28	6.38	1.82	0.41	3.11
2	Oil	1.10	88.58	8.10	0.63	0.26	2.43
	Asphaltene	0.87	89.87	6.52	0.73	0.37	2.51
2A	Oil	1.12	89.22	8.30	0.81	0.24	1.43
	Asphaltene	0.86	89.69	6.46	1.32	0.39	2.14
2B	Oil	1.08	88.97	8.02	2.38	<0.15	~ 0.48
	Asphaltene	0.87	89.35	6.47	1.13	0.37	2.68
3	Oil	1.12	87.49	8.20	0.15	<0.15	~ 4.01
	Asphaltene	0.88	88.28	6.49	1.70	0.40	3.13
3A	Oil	1.18	83.70	8.26	0.37	0.23	7.44
	Asphaltene	0.87	87.96	6.38	1.49	0.46	3.71

With the exception of Run 1, which involved distillations at atmospheric pressure, the H/C atom ratios were almost the same for all of the oil samples, and almost the same for all of the asphaltene samples. The S contents of all fractions were lower than that of the SRC feed, which occasions no surprise. Furthermore, within the limitations of the lower bound for the S analyses, all oil samples had approximately the same S content, as was also true for all asphaltene samples.

The interesting features of the elemental analyses relate to the questions of N elimination and of O elimination from the SRC as a function of catalyst. The average N elimination for Series 1 (blank) was 9%; for Series 2 (SnCl_2), 38%; and for Series 3 ($\text{Co/Mo/Al}_2\text{O}_3$), 1%. The rank ordering, therefore was $\text{SnCl}_2 > > \text{No catalyst} > \text{Co/Mo/Al}_2\text{O}_3$ for effectiveness in N elimination. The average O elimination for Series 1 was 57%; for Series 2, 69%; and for Series 3, 42%. Again the rank ordering is $\text{SnCl}_2 > \text{No catalyst} > \text{Co/Mo/Al}_2\text{O}_3$.

Table III compares results reported by Yen et al. (1976) for the hydrogenolysis of Kentucky coal with those obtained in the present studies for the hydrogenolysis of SRC made from Kentucky coal. The same autoclave (Magnedash) and conditions were used in both studies; tetralin was used as solvent in both cases; and the $\text{Co/Mo/Al}_2\text{O}_3$ catalyst was the same batch of Harshaw 0402T in both cases.

Table III
Comparison of Coal and SRC

Quantity	Coal*		SRC**	
	Blank Run	Co/Mo/Al ₂ O ₃	Blank Run	Co/Mo/Al ₂ O ₃
% S in Oil	0.25	0.21	0.18	<0.19
% S in Asphaltene	0.27	0.47	0.40	0.43
($\frac{\text{Oil}}{\text{Oil} + \text{Asphaltene}}$)	34	49	19	5

*Data from Yen et al. (1976). "Blank Run" = Run T-3; "Co/Mo/Al₂O₃" = Run T-4.

**Present work. Data given are average values for Runs 1 and 1A for "blank", Runs 3 and 3A for "Co/Mo/Al₂O₃"; see Table IV.

The S contents in both the oil and the asphaltene fractions were slightly lower in the SRC runs than in the corresponding fractions from whole coal. This is not surprising, of course, since the organic S of the coal is already significantly reduced in the process of making SRC. It is surprising that (1) the oil production in the SRC runs (cf. Table IV) was exceptionally low relative to the runs with whole coal, and (2) the oil production from SRC was even lower in the presence of Co/Mo/Al₂O₃ than with no catalyst. Two implications may be suggested:

1. The lower oil production from SRC is consistent with the notion, now generally accepted, that the ash in the coal is catalytically active and its removal is harmful (cf. "SRC I" vs. "SRC II" processes). This result is reminiscent of that reported by Weller and Pelipetz (1951). In the earlier work it was found that under identical experimental conditions with no added catalyst, whole Pittsburgh seam coal showed 50-60% conversion, whereas low-ash (1.4%) hand-picked anthraxylon from the same mine showed only 30% conversion. Since iron pyrite is so important an ash constituent in high-ash coals, this again is not surprising: (a) the commercial development of the Bergius process by I.G. Farbenindustrie included Luxmasse, a high-iron material, in the coal-oil paste; (b) impregnated iron sulfate is known to be an excellent catalyst for coal liquefaction (Weller and Pelipetz, 1951a).
2. The deleterious effect of Harshaw Co/Mo/Al₂O₃ on oil production from SRC, relative to no added catalyst, may reflect an undesired polymerization of feed or products occurring as a result of the acidic support (silica-stabilized alumina). Variation of the support acidity was not studied in the present work, but it should be examined.

Table IV summarizes the material balances, total "liquefaction", and the oil and asphaltene distributions for the individual runs.

Table IV

Product Distributions*

Run No.**	Total Products Recovered (g.)	% Liquefaction***	Oil, % of Total Products	Asphaltene, % of Total Products	(Oil) x 100 (Oil + Asphaltene)
1****	61.7	Not detnd.	22.1	77.4	22.2
1A	64.8	93.7	14.0	77.2	15.4
2	50.5	100.0	13.5	86.5	13.5
2A	56.3	99.6	21.8	77.5	22.0
2B	59.8	99.8	20.5	79.1	20.6
3	67.6	94.5	2.7	90.1	2.9
3A	69.9	94.1	5.9	87.2	6.3

*75g. SRC + 300g. tetralin charged in each run.

**See Table I for identification.

***% Liquefaction = $\frac{75 - \text{Toluene insolubles (including catalyst)}}{75} \times 100$

****Distillations in Run 1 made at atmospheric pressure. Vacuum distillation (30-35 Torr.) under N₂ used in all other runs.

Two points should be noted:

1. Although the liquefaction is high in all cases, it is highest in the SnCl₂ runs. (Note: Correction for the catalyst in the toluene insolubles would increase the % Liquefaction to 95.8% in Run 3 and 95.5% in Run 3A. The very small amount of toluene insolubles in Runs 2, 2A, and 2B means that the SnCl₂ has been somehow "solubilized"; it is not present in the toluene insolubles.)
2. Although the material balances are low in all cases, they are consistently lower in the SnCl₂ runs. The losses are tentatively attributed to low-boiling liquid products from the SRC which are lost to the overhead during the toluene and tetralin distillations. The particularly high losses in the SnCl₂ runs are consistent with (a) the higher H₂ consumptions observed in these runs (Table I), and (b) the evidence for many low-boiling constituents in the recovered oil fractions (cf. Figures 2 and 3, below). If this interpretation is correct, then the attribution of the "missing" material to distillation of low-boiling fractions of the oil product would mean that all the oil recoveries listed in Table IV may be lower than the true values. This would be particularly true for the SnCl₂ runs.

Figures 2 and 3 are illustrative of the gas chromatograms obtained on the oil fractions. Figure 2 is for the oil from Run 2A (SnCl₂); Figure 3 is for the oil from Run 3A (Co/Mo/Al₂O₃). In both cases there was some residual

(unstripped) solvent, typically a mixture of tetralin and naphthalene. In both cases there was a major, sharp peak with a retention time of 13.5 minutes (at 270°C.) in this temperature-programmed chromatogram. The identity of this component is unresolved. However, correlations of relative retention time vs. carbon number and vs. normal boiling point were used to predict that the 13.5 minute peak could correspond to a compound analogous to an alkane of carbon number C_{20} - C_{21} and a normal boiling point of ca. 365°C. The sharpness of the peak and the estimated carbon number make it tempting to attribute the peak to some dimeric (i.e., C_{20} , with $M \approx 260$) species originating from the tetralin solvent, and not from the SRC. Our determinations, by vapor-phase osmometry, of the molecular weight of the total oil fractions routinely showed an average molecular weight in the range 250-300. The rich mixture of peaks in the $SnCl_4$ run (Figure 2) between naphthalene and the "13.5 minute unknown" presumably represents low-boiling products in the oil, derived from the SRC with $SnCl_4$ catalyst. It is noteworthy that these peaks are almost absent in the $Co/Mo/Al_2O_3$ run (Figure 3). As pointed out above, the chromatogram shown in Figure 2 is consistent with the high H_2 consumption and the very low material balances when $SnCl_4$ is used. Oil constituents with retention times longer than 13.5 minutes at 270°C., the highest temperature chosen for use with the OV-101 columns, would not have been detected; the G.C. analysis was terminated at this point.

Acknowledgment

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Illustrations

Figure 1. Analytical Procedure

Figure 2. Chromatogram of Oil Fraction from Run 2A

Figure 3. Chromatogram of Oil Fraction from Run 3A

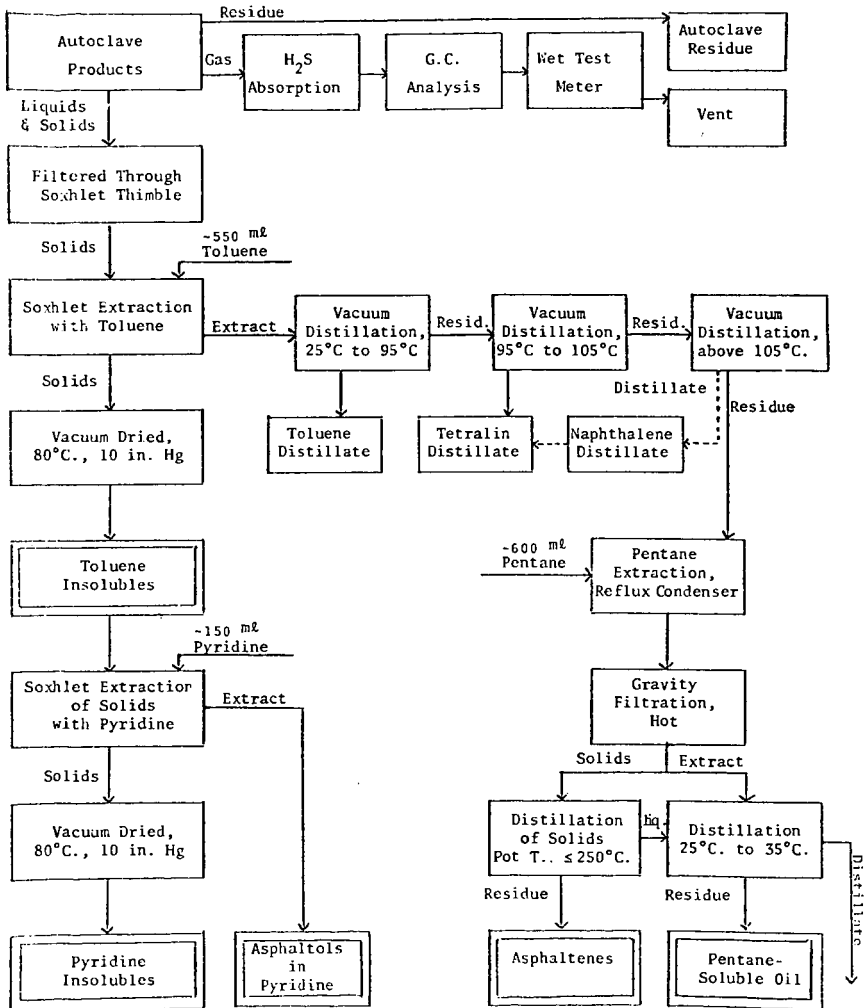


Figure 1. Analytical Procedure

Figure 2
SRC Run #2A Oil Fraction
(1 Time Unit = 0.5 Minutes)

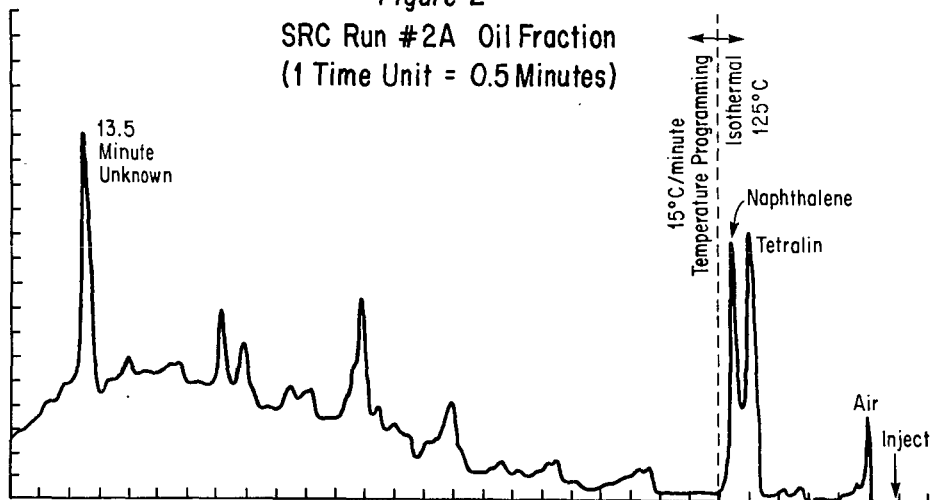
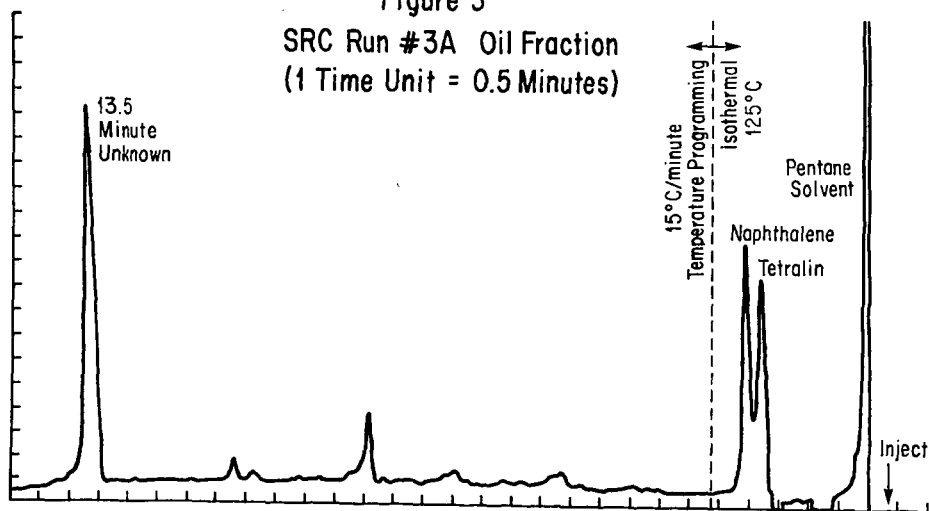


Figure 3
SRC Run #3A Oil Fraction
(1 Time Unit = 0.5 Minutes)



UPGRADING OF SOLVENT REFINED COAL

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INTRODUCTION

Several coal liquefaction processes are being developed by various organizations. The initial objective appears to be the production of low-sulfur boiler fuels for power generation, but it is obvious that upgrading of these coal liquids will be necessary to make acceptable quality fuels for home, transportation, and industrial sectors of our economy. Studies have been conducted on the upgrading of coal-derived liquids, tar, and anthracene oil in the past. More recently, Eisen (1) hydrogenated syncrudes from a western Kentucky coal and a Utah coal in an attempt to prepare gas turbine engine fuel. Stein et al. (2) reported their exploratory studies on hydroprocessing of Solvent Refined Coal (SRC), H-Coal, and SYNTHOIL. Several institutions are also stepping up their activities in coal liquids upgrading, as evidenced by a recent symposium (3).

This report presents an evaluation study on hydroprocessing of a blend of 30 weight percent SRC and 70 weight percent SRC process solvent. It was chosen as the feed-stock, because in some respects it is typical of coal liquids such as SYNTHOIL or mixtures of atmospheric bottoms and vacuum bottoms of H-Coal. They have similar boiling point ranges and high percentages of asphaltenes, organic sulfur and nitrogen. The single-stage hydrotreating of the SRC liquid over conventional nickel-tungsten or nickel-molybdenum catalysts does not give very effective hydrogenation even under severe conditions, whereas the hydrogenation effect, as measured by the increase of H/C atomic ratio, N-removal, and S-removal, is substantially improved in the second-stage hydroprocessing of the hydrotreated SRC liquid.

EXPERIMENTAL

The hydroprocessing of coal liquid was studied in a 500-ml magnetically-stirred autoclave. A series of factorial experiments for single-stage hydrotreating of SRC liquid was conducted using Ni-W supported on silica-alumina (Harshaw Ni-4301E) as the catalyst. The feed was a blend of 30 parts SRC solid and 70 parts SRC solvent, with 5 parts of catalyst added per hundred parts of the feed. Ranges of conditions were: temperature 375°-475°C, initial H₂ pressure 600-1,800 psig (to give operating pressure 900-2,900 psig at reaction temperatures), and reaction time 1-4 hours. The autoclave was stirred at 600-700 rpm during the reaction. The reaction time was measured after the autoclave reached the reaction temperature in about 60-70 minutes, and the autoclave was quenched rapidly after the reaction by an internal water cooling coil. Total products were filtered to obtain liquid oils. Asphaltenes and benzene insolubles were determined according to procedures established by the Chemical and Instrumental Analysis Division of the Pittsburgh Energy Research Center (4). Boiling range distributions of selected oil products were obtained by gas chromatography (ASTM D2887). Gaseous products were analyzed by mass spectrometry.

Various commercial catalysts have been tested for comparison. Most catalysts, excepting ZnCl₂ and noble metal catalysts, were reduced, sulfided, and crushed to pass through a #60 mesh sieve prior to use.

For a two-stage hydroprocessing, the SRC blend was hydrotreated over a Ni-Mo catalyst (Nalco NM-504), in the first stage, in a 5-liter rocking autoclave. The product was then hydroprocessed over a Ni-W catalyst (Harshaw Ni-4301) in the 500-ml magnetically stirred autoclave. The experimental conditions are described further on.

RESULTS AND DISCUSSION

Single-Stage Hydrotreating. Table 1 shows the design and the results of a series of factorial experiments with three variables of temperature, initial H_2 pressure, and time at three levels. The experiments were carried out in random order. The feed was a blend of SRC solid and SRC process solvent (for the composite analyses, see Table 6), and the catalyst was Ni-W supported on silica-alumina (Harshaw Ni-4301E). The data analysis was made by computer, and the dependence of various measured characteristics (Y), such as conversion of pentane insolubles, C_1 - C_4 hydrocarbon yield, S-reduction, N-reduction, oil viscosity, and H_2 consumption on processing variables (X) of pressure, temperature, and time was represented by the following quadratic polynomial

$$Y = \beta_0 + \sum \beta_{1i} X_i + \sum \beta_{ij} X_i^2 + \sum \beta_{ijk} X_i X_j X_k$$

The statistical significance of the regression coefficients (β) has been tested, and it was observed that, except for N-reduction and viscosity, most characteristics correlate well and pass the F-test for fit with 95% confidence. The quadratic approximation yielded plots showing the effects of initial H_2 pressure and temperature on the conversion of pentane insolubles (benzene insoluble + asphaltene) and on S-reduction in Figures 1 and 2, respectively.

Further, this equation can be used to represent characteristic response surfaces during an optimization analysis. The analysis is made by finding an optimum point over the response surface of the characteristic being optimized, while simultaneously keeping other characteristics within specified levels. The main objective of the coal liquids upgrading in the first stage of a two-stage concept is hydrosulfurization and hydrodenitrogenation. These reactions can be better achieved at higher temperatures, but H_2 consumption and C_1 - C_4 hydrocarbon formation could become uneconomically high. Table 2 shows the optimum conditions for (1) achieving a maximum S-reduction while limiting H_2 consumption to 2.8 weight percent (1740 scf/bbl) and C_1 - C_4 yield to 5 weight percent, (2) achieving a minimum C_1 - C_4 hydrocarbon formation while realizing S-reduction of at least 80% and N-reduction of 35%, and (3) achieving a maximum conversion of pentane insolubles without any characteristic constraints. It appears that temperature is the controlling factor for achieving a desired optimum. Figure 3 shows the change of various characteristics with temperature at an optimum condition of 1,800 psi and 3.18 hours.

Elemental analyses were obtained for some selected oil products. In general, the hydrotreated products were not sufficiently rich in hydrogen, and N and O contents were still too high. The S-removal was relatively satisfactory. Figure 4 shows that the H/C ratio increases only from 0.92 to 1.1, regardless of the increase in H_2 consumption. It appears that, under severe conditions at high temperatures, additional H_2 is consumed in C_1 - C_4 hydrocarbon gases formation. The decrease of the N/C ratio is only moderate with rising H_2 consumption.

Various hydroprocessing catalysts (Table 3) were evaluated at one standard set of conditions used in the factorial experiments. The results in Table 4 show that Ni-Mo type catalyst exhibited the best overall activity.

TABLE 1. Factorial experiments - hydrotreating SRC liquid with Ni-W catalyst

Controlled factors			Measured characteristics					
Pressure psi	Temp, °C	Time hr	Pentane insoluble conversion, wt %	C ₁ -C ₄ yield, wt %	% S reduction	% N reduction	Viscosity, cs at 60°C	H ₂ Consumed, wt %
600	375	2.5	10.2	0.6	40.9	9.8	113	0.43
1800	375	2.5	23.4	0.9	60.0	19.6	66	1.10
600	475	2.5	-65.6	12.7	63.5	21.0	65	1.16
1800	475	2.5	65.8	13.5	89.6	31.5	4.3	3.76
600	425	1	20.9	2.2	46.1	3.9	58	0.71
1800	425	1	48.6	2.3	72.2	21.7	18	1.69
600	425	4	4.6	6.7	53.0	5.6	33	1.11
1800	425	4	73.7	5.3	86.1	41.3	6.2	3.08
1200	375	1	-3.8	0.4	42.6	7.7	183	0.60
1200	475	1	1.5	10.3	61.7	10.5	45	1.85
1200	375	4	24.5	0.8	60.0	18.2	59	1.18
1200	475	4	8.9	14.8	77.4	23.8	37	2.94
1200	425	2.5	53.7	2.9	73.9	21.0	14	1.51
1200	425	2.5	45.0	3.6	68.7	22.4	14	1.73
1200	425	2.5	50.3	3.7	73.9	21.0	14	1.67

TABLE 2. Characteristic optimization

	Value at maximum % S-reduction	Value at minimum C ₁ -C ₄ yield	Value at maximum PI conversion
Factors			
Pressure, psi	1800	1800	1800
Temperature, °C	429.2	406.4	438.4
Time, hr	3.12	3.18	4
Characteristics			
S-reduction, %	86.4	80 ^a	88.8
N-reduction, %	38.0	36.8 ^a	38.6
Pentane insoluble conversion, %	80.8	66.7	85.6
C ₁ -C ₄ yield, wt %	5 ^a	2.4	7.4
H ₂ consumed, wt % (scf/bbl)	2.8 ^a (1740)	2.2 (1360)	3.5 (2170)

^a Limiting characteristics in optimization.

TABLE 3. Hydroprocessing catalysts

Catalyst No.	1	2	3	4	5	6	7	8	9
	Harshaw Ni-4301	Harshaw Ni-4303	Harshaw 0402T	Harshaw HT-100E	Nalco NM-504	Girdler T-826	Harshaw Pd-0501	Linde SK-120	Girdler T-309B
Chemical composition, wt. %									
NiO	6 ^a	6 ^a	-	3.8	5.5	2.5	-	-	-
WO ₃	19 ^a	19 ^a	-	-	-	-	-	-	-
CoO	-	-	3	-	-	2.5	-	-	-
MoO ₃	-	-	15	16.8	19	10	-	-	-
Pd	-	-	-	-	-	-	0.3	0.5	-
Pt	-	-	-	-	-	-	-	-	0.5
P ₂ O ₅	-	-	-	-	7	-	-	-	-
SiO ₂	50	-	5	1.5	1.6	-	-	64.5	-
Al ₂ O ₃	25	75	77	78	64	85	99.7	22.7	99.5
RE ₂ O ₃	-	-	-	-	-	-	-	10.7	-
Physical properties									
Surface area, m ² /g	228	152	200	175	170	232	186	> 550	190
Pore volume, cc/g	0.37	0.54	0.4	0.54	0.41	-	0.38	-	0.27
Avg. pore diameter, Å	65	142	100	123	97	-	82	-	57

^a Values listed are metal contents of Ni or W.

TABLE 4. Comparative performance of catalysts

Catalyst No.	Type	(1,800 psi, 425°C, 1 hr)									
		Pentane insoluble conversion, wt %	Bottom (480°C+) wt %	350°C-C ₁ -C ₄ yield, wt %	% S reduction	% N reduction	H ₂ consumed, wt %	Viscosity, cs at 60°C			
1	NiW on silicated alumina	48.6	83.8	58.3	2.32	72.2	21.7	1.69	18.0		
2	NiW on alumina	57.4	87.0	58.2	1.70	75.7	21.6	1.88	18.0		
3	CoMo on silicated alumina	52.6	85.7	60.5	1.94	63.5	16.7	1.60	21.7		
4	NiMo on silicated alumina	60.3	82.5	59.1	1.66	73.9	27.2	2.03	14.5		
5	NiMo on P ₂ O ₅ -alumina	63.0	83.7	56.6	2.03	77.4	30.0	2.08	13.6		
6	NiCoMo on alumina	55.3	87.4	61.4	1.82	68.7	15.3	1.90	19.0		
7	Pd on alumina	15.7	91.8	60.7	1.76	28.7	2.0	1.23	54.1		
8	Pd on Y-type molecular sieve	24.9	85.0	57.3	2.30	27.0	16.7	1.32	44.2		
9	Pt on alumina	12.4	75.2	46.7	1.86	30.4	2.0	1.12	47.6		
10	ZnCl ₂	64.9	86.5	59.1	2.39	37.4	38.4	2.11	10.7		
11	None	-10.2	8.2	40.3	1.53	13.0	-	0.40	172		

Two-Stage Hydroprocessing. A two-stage hydroprocessing was conducted. In the first stage, the SRC blend was hydrotreated in a 5-liter rocking autoclave at an initial H_2 pressure of 2,200 psi and 415°C for 4 hours. It was judged that this condition would give a good compromise of high S and N reduction with low H_2 consumption and C_1 - C_4 yield. The catalyst was Ni-Mo on alumina promoted with P_2O_5 and SiO_2 (Nalco NM-504). The product was then used as the feedstock for a hydrocracking study over Ni-W catalyst on silica-alumina (Harshaw Ni-4301). A series of factorial experiments for this second-stage hydrocracking was conducted at 1,800 psi initial H_2 pressure, with temperature in the range of 377°-433°C and reaction time in the range of 40-180 minutes. The results of the factorial experiments are shown in Table 5. Some results of using catalysts other than Ni-W are also included. Through a computerized regression analysis of the second-stage hydrocracking data, we were also able to determine that most characteristics, such as pentane insoluble conversion, S-reduction, N-reduction, H_2 consumption, and C_1 - C_4 hydrocarbon yield, could be represented by the quadratic approximation. Figure 5 shows the change of characteristics with temperature for the second-stage hydrocracking at the specified conditions. It is evident that the upgrading is quite effective at the second stage. The benefit of the second-stage hydroprocessing can be better seen in Table 6, which shows the analyses of products obtained from a two-stage hydroprocessing of the SRC blend. The light fractions (IBP-260°C and 260°-350°C, obtained from a Kontes vacuum distiller) of the second-stage product have very low sulfur and nitrogen contents (pass EPA specifications for turbine oil).

Additional experiments were also made to determine the effect of pressure (Figure 6) in the second-stage hydrocracking. As expected, the hydrocracking effect improved with increasing pressure.

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Reference to a company or brand name is made to facilitate understanding and does not imply endorsement by the U.S. Department of Energy.

TABLE 5. Factorial experiments - second stage hydroprocessing with Ni-W catalyst

(1800 psi initial H ₂ pressure)									
Temp, °C	Time, min	Pentane		350°C-- yield, wt %	C ₁ -C ₄ yield, wt %	% S reduction	% N reduction	H ₂ consumed, wt %	Viscosity, cs at 60°C
		insoluble conversion, %	soluble conversion, %						
377	110	22.9	71.7	0.1	44.4	38.2	0.76	7.8	
385	60	12.4	67.5	0.1	22.2	30.2	0.58	8.2	
385	160	38.3	65.6	0.1	55.6	41.9	0.94	6.7	
405	40	9.8	61.5	0.1	66.7	33.7	0.58	7.5	
405	110	41.4	58.7	0.4	44.4	47.7	0.91	6.1	
405	110	33.9	71.8	1.1	44.4	54.7	1.00	6.1	
405	110	42.1	62.7	1.0	33.3	55.8	1.13	6.1	
405	180	41.8	69.9	1.1	66.7	61.6	1.35	5.0	
425	60	45.7	65.8	1.2	55.6	46.5	0.85	5.3	
425	160	56.6	66.8	2.0	55.6	66.3	1.70	3.6	
433	110	55.5	64.9	2.1	44.4	59.3	1.55	3.7	
Catalyst effect									
425 ^a	160	60.4	65.0	1.94	66.7	51.2	1.47	3.7	
425 ^b	160	10.5	64.9	2.29	55.6	74.4	1.87	3.5	
425 ^c	160	51.2	70.3	1.96	55.6	34.9	1.10	4.4	

^a Co-Mo on alumina, Girdler G-51.^b Pd on molecular sieve, Linde SK-120.^c Pt on alumina, Girdler T3093.

TABLE 6. Two-stage hydroprocessing of SRC liquid

	SRC ^a blend	First-stage ^b hydroprocessed product	Second-stage ^c hydroprocessed product			
			Overall	IBP- 260°C	260°- 350°C	350°C+
Composition, wt %						
Oil	69.50	93.8	96.7			
Asphaltene	19.58	6.1	3.3			
Benzene insol	10.92	0.1	-			
Fraction, wt %						
IBP - 260°C	5.93	21.92	29.54			
260°C - 350°C	17.70	39.74	45.19			
350°C +	76.36	38.34	25.28			
Elemental analysis, wt %						
C	88.19	89.20	89.29	88.46	89.93	90.31
H	6.78	8.47	9.36	11.13	9.46	8.00
N	1.43	0.84	0.51	0.04	0.11	0.75
S	0.58	0.10	0.049	0.035	0.048	0.113
O	2.89	1.39	0.79	0.34	0.55	0.82
Ash	0.13	-	-	-	-	-
H/C atomic ratio	0.92	1.20	1.26	1.51	1.26	1.06
Specific gravity, 15/15°C	1.122	1.023	0.980			
Viscosity, cs at 60°C	450	39.8	5.0			

^a SRC blend contains 30 parts SRC solid and 70 parts SRC solvent.

^b Hydroprocessed at 1800 psi, 415°C and 4 hours with Ni-Mo.

^c Hydroprocessed at 1800 psi, 405°C and 3 hours with Ni-W.

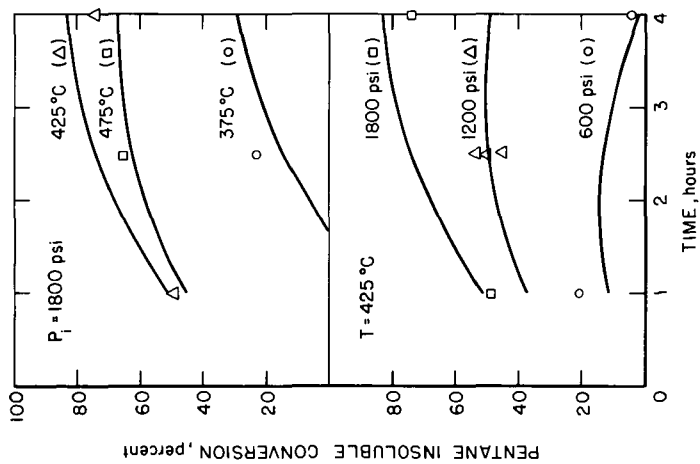


Figure 1—Effects of pressure and temperature on pentane insoluble conversion.

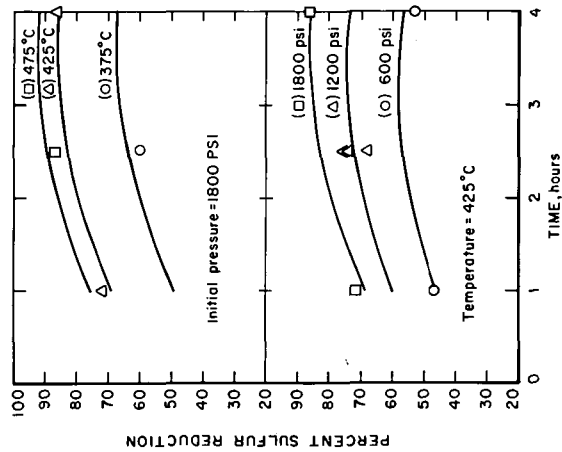


Figure 2—Effects of pressure and temperature on sulfur reduction.

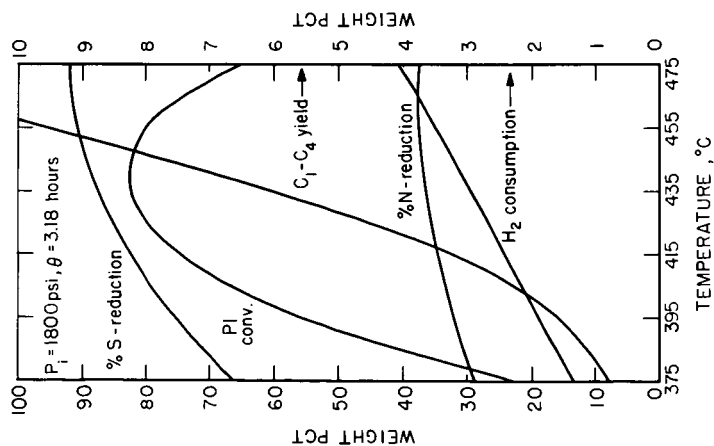


Figure 3—Change of characteristics with temperature.

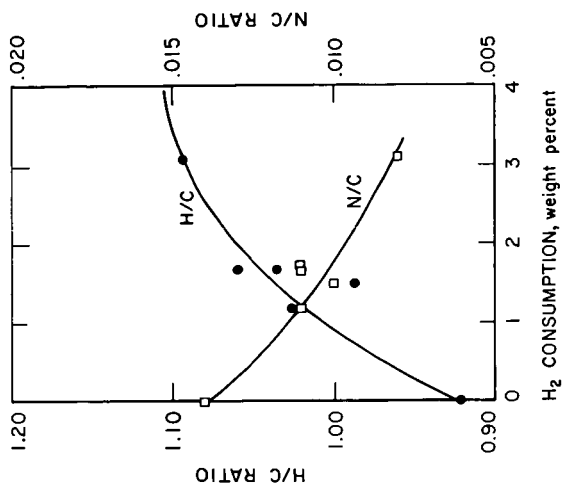


Figure 4—Change of H/C and N/C ratios with H₂ consumption.

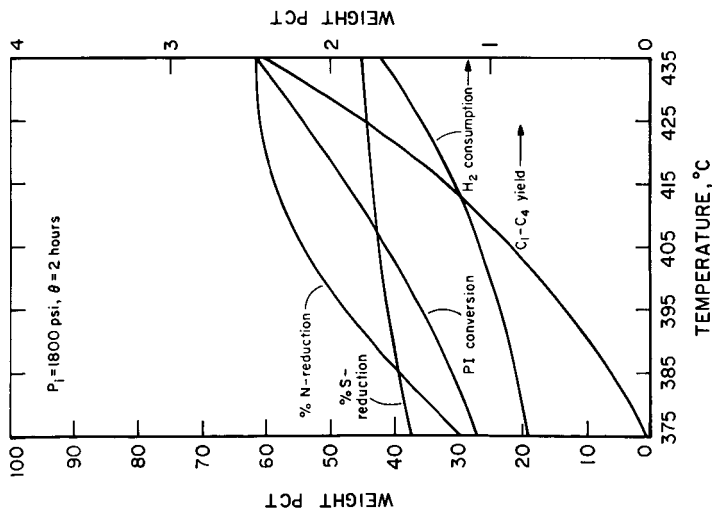


Figure 5—Change of characteristics with temperature for second-stage hydrocracking.

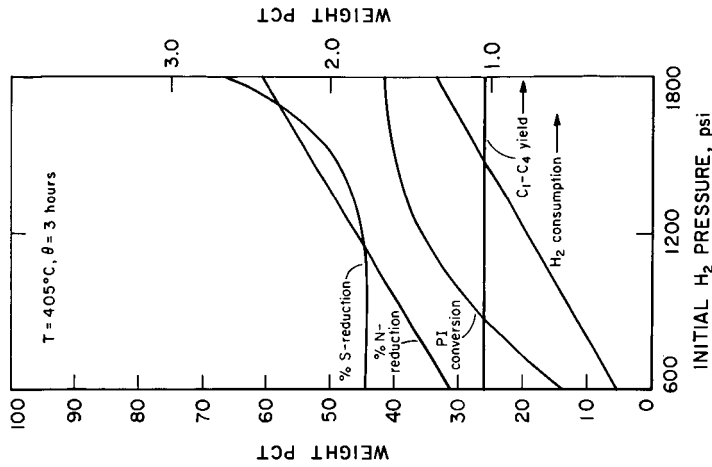


Figure 6—Effect of pressure in second-stage hydrocracking.

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The Sulfided Co-Mo/ γ - Al_2O_3 Catalyst: Evidence of Structural Changes During Hydrodesulfurization of Dibenzothiophene

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Introduction

The catalyst most often used for hydrodesulfurization (HDS) of petroleum fractions are derived from oxides of Co and Mo supported on γ - Al_2O_3 , and their surfaces are sulfided prior to operation. Structures of the oxidic and sulfidic forms of the catalyst are incompletely understood and much debated (1-3), and since the available structural information has been derived from studies of catalysts at conditions far removed from those of commercial operation (about 50-200 atm and 350-320°C), it is not clear how operating variables influence the catalyst structure and activity in practice.

The hydrodesulfurization kinetics data reported here were measured to characterize the catalyst operating at about 100 atm and 300°C; the reactant stream contained dibenzothiophene (DBT) and hydrogen dissolved in n-hexadecane carrier oil. The results provide the first evidence of structural variations in the Co-Mo/ γ - Al_2O_3 catalyst brought about by changes in the reaction environment.

Experimental Methods

The catalyst used in all experiments was American Cyanamid HDS 16A having the following properties (prior to sulfiding): surface area, 176 m^2/g ; pore volume, 0.50 cm^3/g ; Co content, 4.4 wt%; and Mo content, 7.5 wt%. A sample of 10 mg of catalyst powder (80-100 mesh particles, demonstrated experimentally to be small enough to ensure the lack of intraparticle diffusion resistance) was charged to the reactor, and the catalyst was sulfided at 400°C for 2 h with a flow of about 40 cm^3/min of 10% H_2S in H_2 at atmospheric pressure. Following the sulfiding, the flow of feed liquid was started. The feed contained 0.12 wt% DBT (Aldrich, 95% purity) in n-hexadecane [Humphrey Chemical Co. (redistilled)], and it was saturated with H_2 at 68 atm and room temperature. Occasionally, the feed was saturated with H_2S at various partial pressures before it was saturated with H_2 . Experiments were carried out with a flow reactor described in detail elsewhere (4). The reactor operated at 300°C and 104 atm. Under all reaction conditions, the fractional conversion H_2 was < 5%, so the H_2 concentration could be considered to be virtually constant throughout the reactor.

Liquid product samples were collected periodically (without interrupting the reactant flow) and analyzed by glc (5). DBT and H_2 were converted into biphenyl and H_2S . To a first approximation, these were the only products formed; the detailed reaction network is considered separately (6).

Results

Some conversion data are plotted in Fig. 1. They show that the initial conversion at a relatively high inverse space velocity (proportional to reactant-catalyst contact time) increased about 10% over the first 10-20 h of operation, following by nearly constant conversion (referred to as "lined-out conversion") for 150 h or more. When the lined-out conversion was determined for various space velocities, the reaction was found to be pseudo-first-order in DBT (5).

Figure 1 shows the results of variations in the space velocity caused by changes in the feed flow rate. After the first step change in feed flow rate, there was a change in conversion characterized by a transient period of some 50 h before the catalyst achieved another time-invariant activity. After a second change in space velocity at 70 h onstream time, giving again the original value, there followed a transient period, as expected, but, surprisingly, the catalyst failed to return to its original lined-out activity.

In further experiments, each begun with a fresh catalyst charge, increasing concentrations of H_2S were added to the feed. The data of Fig. 2 show that at low H_2S concentrations [$(H_2S)/(H_2)$ in the feed liquid - 0.015], the qualitative pattern of changes mentioned above again occurred. The catalyst activity in the presence of added H_2S at each space velocity appeared to be less than that in the absence of added H_2S , corresponding to the well-known inhibition of reaction by H_2S (1, 6). When higher feed concentrations of H_2S were used, the transient periods of change in the catalyst activity became shorter; when the $(H_2S)/(H_2)$ ratio in the feed was as great as 0.2, the transients in catalyst activity were virtually eliminated.

In summary, these results show that H_2S does more than just inhibit the HDS reaction by adsorbing on catalytic sites in competition with DBT. We infer that when the space velocity was increased, reducing the concentration of H_2S produced in the reaction (Figs. 1 and 2), structural changes took place, reducing the number of catalytic sites. The presumed solid-state reactions were slow, in contrast to the adsorption of H_2S that caused the inhibition of reaction. The loss of catalytic sites was only partially reversed when the concentration of H_2S was again increased by decreasing the space velocity. But when H_2S was present in the feed in sufficient amounts that the H_2S concentration remained nearly constant throughout the reactor, then the catalyst activity (and structure) did not change with space velocity; the data then indicate only the simple competitive inhibition of reaction by H_2S , and there was no hysteresis.

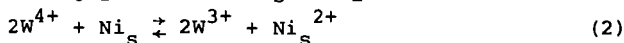
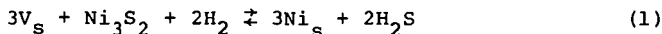
The foregoing results suggest that there is an optimum concentration of H_2S [or perhaps a $(H_2S):(H_2)$ ratio] corresponding to a catalyst structure which has a maximum HDS activity. Experiments were carried out to test this suggestion. In one series, catalyst were brought on stream with initially low space velocities, producing initially high activities; the experiments were done with various feed H_2S concentrations. The pseudo-first-order rate constants (determined from linear semilogarithmic plots of fraction unconverted vs. inverse space velocity) are represented by curve B in Fig. 3; they indicate that in these experiments the H_2S was simply a reaction inhibitor.

In the complementary series of experiments, each new catalyst charge was brought on stream at a high space velocity and, correspondingly, with a relatively low conversion and a low H_2S concentration; H_2S concentration in the feed was varied systematically. The rate constants scatter around curve A in Fig. 3. These results confirm that increasing the H_2S concentration increased the activity of the catalyst when it was brought on stream in such a way that its initial activity was relatively low.

The important conclusion is that the catalyst achieves a lined-out activity which is dependent on the reactor startup procedure (and probably on the presulfiding procedure as well). This conclusion may be important to the technology of HDS, and we suggest that the industrial art may include the application of presulfiding and reactor startup procedures which maximize the catalyst activity; the optimum startup would ensure that some H_2S contacted the catalyst initially.

Discussion

The observed changes in catalytic activity and, by inference, catalyst structure, are suggestive of Farragher's (7) observations of the activity of $Ni-W/\gamma-Al_2O_3$ catalyst for benzene hydrogenation. Farragher presented evidence of hysteresis effects similar to those reported here, but caused by temperature variations; he explained the results in terms of solid-state reactions influencing catalyst structure and activity. The suggested reactions were the following:



The former reaction involves conversion of Ni from bulk Ni_3S_2 on the catalyst; it becomes intercalated in interstitial octahedral holes at the surface of WS_2 crystallites on the catalyst surface. The latter reaction is believed to produce W^{3+} ions at the surface, which Voorhoeve et al. (8,9) have characterized by esr and identified as the catalytic sites for benzene hydrogenation. Farragher showed that both the rate constant for benzene hydrogenation and the esr signal indicative of W^{3+} were dependent on the P_{H_2S}/P_{H_2}

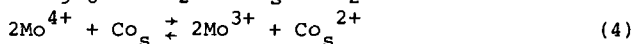
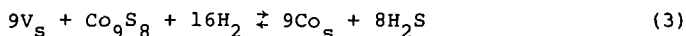
ratio in a way that is consistent with the catalyst stoichiometry suggested in Eqs. (1) and (2).

There is much evidence (1, 11) [but not a consensus (2, 3)] supporting the view that the Co-Mo/ γ -Al₂O₃ catalyst is similar to the Ni-W/ γ -Al₂O₃ catalyst, consisting of MoS₂ and Co₉S₈ on the Al₂O₃ surface, and esr evidence supports the idea that the catalytic sites are Mo³⁺ ions intercalated at the edges of the MoS₂ crystallites (1, 7, 12).

Following Farragher, and assuming the validity of the edge intercalation model for the Co-Mo catalyst, we suggest the following speculative interpretation of the structural changes in the catalyst brought about by changes in the reaction environment. The fully active catalyst is supposed to consist of MoS₂ crystallites intercalated with Co²⁺ ions, and H₂S can bond to the surface at anion vacancies in competition with DBT, causing inhibition of the HDS reaction. When only little H₂S is present, however, intercalated MoS₂ may be converted into a sulfur-deficient layer structure which may lack catalytic activity. We speculate that CoMo₂S₄ may be the sulfur-deficient structure, since it is known to lack HDS activity and to have the layer structure shown in Fig. 4 (10). Here both Co²⁺ and Mo³⁺ ions are octahedrally surrounded by S²⁻ ions, whereas in MoS₂ the surrounding is trigonal prismatic.

It is important that CoMo₂S₄ meets the criterion of having a lower sulfur content than the presumed catalyst, Co-intercalated MoS₂; to explain the observed intermediate activities, we suggest that the catalyst may consist of a range of intermediate structures which could be interconverted by local redistributions of Co and Mo ions accompanied by changes in the Mo-S surrounding.

An explicit suggestion is the epitaxial structure shown in Fig. 5. This structure accounts for the observed promotion by Co at higher Co/Mo ratios than can be accounted for by the edge intercalation model (11). It might be expected to undergo changes analogous to those postulated by Farragher for the Ni-W catalyst:



This model is consistent with the experimental evidence, but it is rough and speculative and in need of experimental evaluation.

Notation

- k pseudo-first-order rate constant, $\text{cm}^3/\text{h}\cdot\text{g}$ of catalyst
 P partial pressure
 V_s interstitial octahedral hole in a layer structure like MoS_2

Acknowledgment

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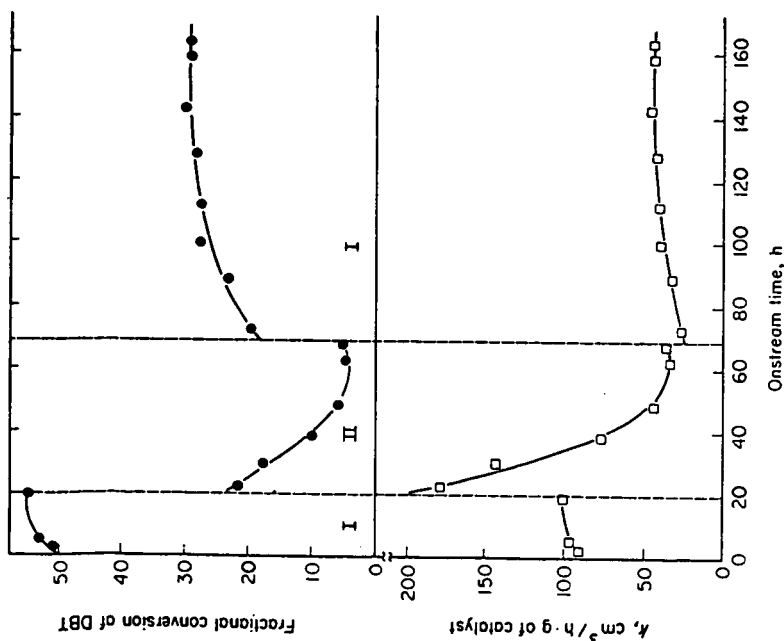


Figure 1. Conversion and pseudo-first-order rate constants for HDS of DBT. I: space velocity = 128 cm³/h·g of catalyst. II: space velocity = 710 cm³/h·g of catalyst. A: feed of DBT in n-hexadecane which had been saturated with H₂ at 25°C and 68 atm. The catalyst was American Cyanamid HDS 16A. Reaction conditions: 300°C and 104 atm.

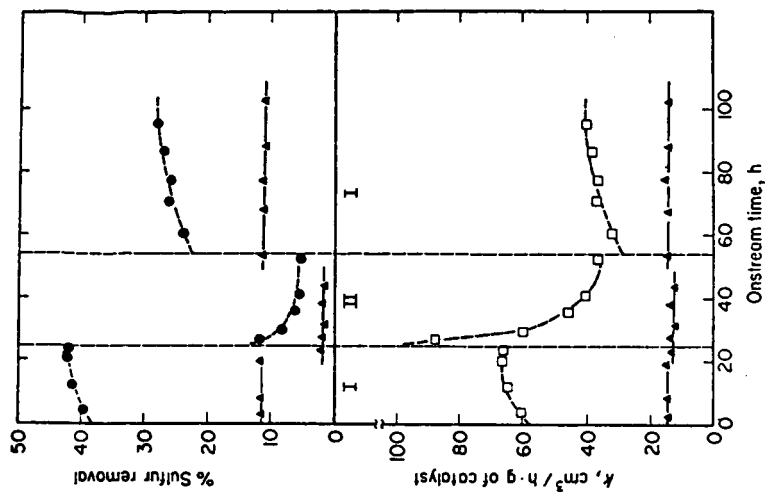


Figure 2. Conversion and pseudo-first-order rate constants for HDS of DBT. I: space velocity = 124 cm³/h·g of catalyst. II: space velocity = 705 cm³/h·g of catalyst. Concentration catalyst = 0.2 (-Δ-); 0.015 (-○-). The feed, catalyst, and reaction conditions were the same as described in the caption of Fig. 1, except for the added H₂.

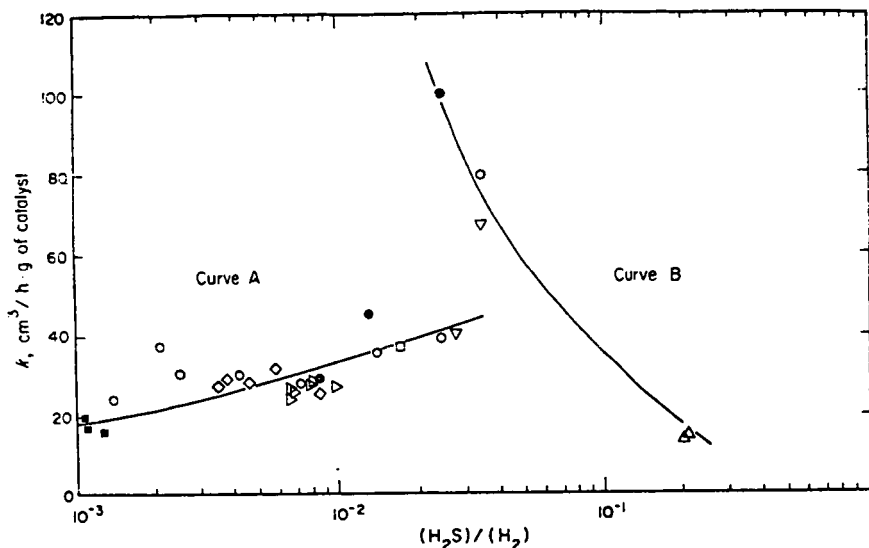


Figure 3. Effects of H_2S on catalyst activity for HDS of DBT at the reaction conditions given in the caption of Fig. 1.

The points on curve A represent conversion measured at various space velocities and with various feed $(H_2S)/(H_2)$ ratios for catalyst which had previously lined out at high space velocities (700^2750 $cm^3/h \cdot g$ of catalyst). These results show that the catalyst which lined out at high space velocities was sulfur deficient and relatively inactive, becoming more active on addition of H_2S , as discussed in the text.

The points on curve B represent conversion measured at various feed $(H_2S)/(H_2)$ ratios for catalyst which had previously lined out at low space velocities ($90-100$ $cm^3/h \cdot g$ of catalyst). These results indicate competitive inhibition of reaction by H_2S .

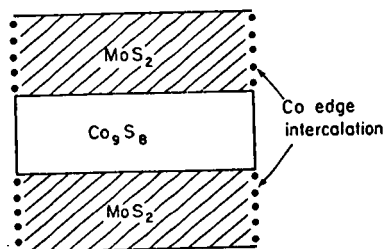


Figure 4. Model of the sulfided Co-Mo- γ - Al_2O_3 catalyst, representing layers of Co_9S_8 and MoS_2 intercalated with Co^{2+} at the crystal edges.

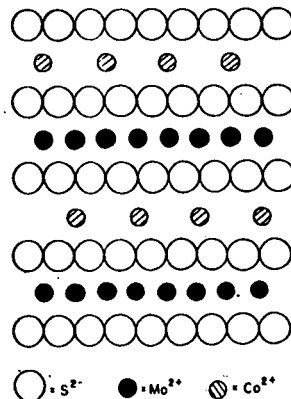


Figure 5. Representation of the layer structure of $CoMo_3S_4$. The actual structure is distorted, as shown by van den Berg [12].

EFFECT OF CATALYST COMPOSITION ON
QUINOLINE AND ACRIDINE HYDRODENITROGENATION

By

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INTRODUCTION

Recently there has been increased interest in the hydrodenitrogenation of nitrogen-containing aromatic compounds typical of those found in petroleum, coal-derived liquids and shale oil. Because of the high nitrogen contents of coal-derived liquids and shale oil, hydrodenitrogenation will become increasingly important in the future. Mars and Coworkers (1-4) have clarified the reaction network and kinetics associated with the hydrodenitrogenation of pyridine. Their work was done on unsulfided Co-Mo/Al₂O₃ catalyst. Although several authors (5-9) have studied hydrodenitrogenation, neither the reaction network, nor the reaction kinetics have been adequately defined for anything but pyridine. We have recently established the reaction networks and reaction kinetics of the hydrodenitrogenation of quinoline (10, 11) and of acridine (12) over sulfided hydroprocessing catalysts under high-pressure liquid-phase conditions.

Both the prior literature and our work shows that hydrodenitrogenation of nitrogen-containing compounds occurs via a complex reaction network involving hydrogenation of the aromatic rings followed by carbon-nitrogen bond breaking. This is in contrast to hydrodesulfurization, in which sulfur removal occurs directly without hydrogenation of the associated aromatic rings (13). It is therefore important to understand how catalyst composition affects the relative rates of hydrogenation and of bond breaking in the complex nitrogen-removal reaction network. This bifunctional nature of the reaction network requires an appropriate balance between the catalyst hydrogenation and catalyst bond-breaking functions to provide the most active catalyst. A quantitative definition of the relative kinetic role of the two catalyst functions in hydrodenitrogenation is not available.

Generally Ni-Mo/Al₂O₃ or Ni-W/Al₂O₃ have been reported to be more active for hydrodenitrogenation than Co-Mo/Al₂O₃, the catalyst of choice for hydrodesulfurization, and the enhanced behavior is often assumed to be due to higher hydrogenation activity (9, 14, 15). This is not confirmed by

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quantitative experimental data, particularly under typical hydroprocessing conditions with multi-ring nitrogen-containing compounds. In this work we have evaluated the relative behavior of commercial hydroprocessing catalysts of differing metal composition and support under high-pressure liquid-phase conditions. The catalysts were examined in the oxidic form, the sulfided form and the sulfided form with H_2S in the system. First-order rate constants for all hydrogenation and bond breaking steps in the reaction networks were determined as a function of catalyst type and catalyst pretreatment. Our objectives were to determine how the catalyst type and pretreatment affected the rate of each individual step in the hydrodenitrogenation reaction network and thus to elucidate the fundamental differences in the catalysts.

EXPERIMENTAL

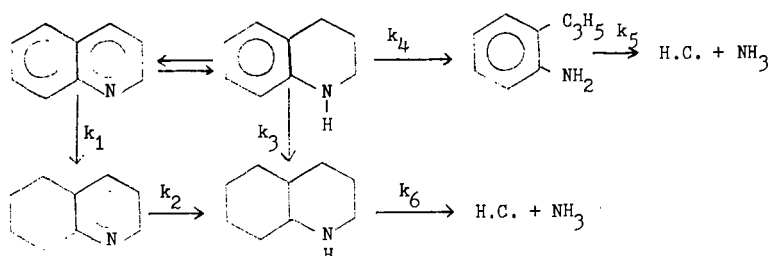
The experiments were carried out in a one-liter stirred autoclave (Autoclave Engineer) with glass liner; the autoclave was operated in batch mode. A special reactant-oil-catalyst injection system was attached to the autoclave to inject catalyst and reactant (nitrogen-containing compound) in carrier oil into the autoclave after it had been stabilized at the operating temperature and pressure. Consequently, the problems of reaction and catalyst deactivation during the long heat-up time frequently encountered in autoclave studies were eliminated, and zero time was precisely defined. The system has been described elsewhere (10, 11); operating conditions were:

Temperature: quinoline, $342 \pm 1^\circ C$; acridine, $367 \pm 1^\circ C$
Total pressure: quinoline, 34 atm; acridine, 136 atm
Reactant concentration: quinoline, 1.0 wt%; acridine 0.5 wt %
Catalyst: 0.5 wt % in carrier oil; 150-200 mesh;
 sulfided (quinoline, 2 hr at $325^\circ C$; acridine 2 hr at
 $425^\circ C$) in 160 cc/min of 10% H_2S in H_2
Carrier Oil: 500 cc highly paraffinic White Oil;
 0.05 wt % CS_2 added to give 1.4 vol % H_2S in the
 gas phase
One-liter autoclave, stirred at 1700rpm

Analysis of reaction products was by G. C. using a 10' X 1/8' Chromosorb 103 glass column for quinoline, a 50m OV101 SCOT glass column for acridine and a nitrogen-specific detector so that individual nitrogen-containing compounds could be identified.

RESULTS

The reaction network for quinoline hydrodenitrogenation with specific rate constants identified, as established by Shih *et al.* (10, 11), is:



The behavior of different catalysts in quinoline hydrodenitrogenation is given in Table I. Ni-Mo/Al₂O₃ is a slightly better catalyst for the removal of nitrogen from quinoline than Co-Mo/Al₂O₃ or Ni-W/Al₂O₃ as shown by the pseudo first-order rate constants for total nitrogen removal. The Ni-containing catalysts appear to be more active for hydrogenating the benzenoid ring (k_1 and k_3); whereas the Mo-containing catalysts appear to be more active in hydrogenating the heteroaromatic ring (k_2). The pseudo first-order rate constants for the cracking steps (k_4 and k_6) are more dependent on the source of the alumina (catalyst) than on the metals present as demonstrated better by other studies not reported here.

TABLE I
HYDRODENITROGENATION OF QUINOLINE OVER DIFFERENT CATALYSTS

Rate constant, min ⁻¹	Ni-Mo/Al ₂ O ₃ (Cyanamid HDS-9A)	Co-Mo/Al ₂ O ₃ (Cyanamid HDS-16A)	Ni-W/Al ₂ O ₃ (Nalco NT-550)
k_1	3.10	1.49	2.17
k_2	1.11	1.51	0.52
k_3	0.63	0.26	0.33
k_4	0.077	0.067	0.073
k_5	0.61	1.51	0.36
k_6	2.54	3.56	1.11
$k_{\text{Total N-removal}}$	0.30	0.20	0.19

Operating conditions: Catalysts were presulfided, no CS₂ added to the system, T = 342°C, P = 34 atm.

Presulfiding has a marked effect on the total nitrogen removal rate (Table II); the rate constant for total nitrogen removal almost doubles. However there seems to be little or no gain in going from the oxidic form to the sulfided form of the catalyst in steps that involve carbon-nitrogen bond breaking. The rates for these steps remain basically the same, as can be seen upon comparing k_5 and k_6 for the oxidic and sulfided catalyst in Table II. Presulfiding has a marked influence on the rate of hydrogenation of the benzenoid and heteroaromatic ring (k_1 , k_2 and k_3). However, there seems to be a preference for hydrogenation of the benzenoid ring over the heteroaromatic ring in quinoline; there is a 4-fold increase in the value of k_1 and k_3 as compared to only a 1.5-fold increase in k_2 . The reaction path involving *o*-propylaniline is of negligible importance for the oxidic form.

TABLE II
EFFECT OF PRESULFIDING ON THE HYDRODENITROGENATION OF QUINOLINE

Rate constant, min ⁻¹	Ni-Mo/Al ₂ O ₃ (Cyanamid HDS-9A)	
	oxidic	presulfided
k_1	0.72	3.10 (4.3X)
k_2	0.75	1.11 (1.5X)
k_3	0.18	0.63 (3.5X)
k_4	0.0023 ^a	0.077
k_5	0.75	0.61
k_6	2.2	2.54
$k_{\text{Total N-removal}}$	0.17	0.3

Operating conditions: catalyst presulfided at 325°C for 2 hr in 10% H₂S/H₂, no CS₂ added, T = 342°C, P = 34 atm.

^aThis value was so small for the oxidic form that its value is uncertain.

The effect of CS₂ (H₂S) on the reaction system is shown in Table III. H₂S increases the rate of total nitrogen removal. The presence of H₂S enhances the carbon nitrogen bond breaking rates (i.e., k_6 and particularly k_4). However, k_5 is negatively affected since the transformation of *o*-propylaniline to a hydrocarbon and ammonia involves first a hydrogenation

step (10, 11); k_5 is a compound pseudo first-order rate constant. Little advantage of having H_2S present is seen in the hydrogenation rates (k_1 , k_2 and k_3). For the Co-Mo/ Al_2O_3 catalyst there is no enhancement of the hydrogenation of the heteroaromatic ring, but the benzenoid ring hydrogenation capacity is slightly enhanced. For the Ni-Mo/ Al_2O_3 and Ni-W/ Al_2O_3 catalysts the converse is true; they experience a decrease in their benzenoid ring hydrogenation activity and an increase in their heteroaromatic ring hydrogenation activity with gas-phase H_2S .

TABLE III

EFFECT OF H_2S ON THE HYDRODENITROGENATION OF QUINOLINE

Rate constant, min ⁻¹	Ni-Mo/ Al_2O_3 (Cyanamid HDS-9A)		Co-Mo/ Al_2O_3 (Cyanamid HDS-16A)		Ni-W/ Al_2O_3 (Nalco NT-550)	
	A	B	A	B	A	B
k_1	3.10	3.09	1.49	1.51	2.17	1.71
k_2	1.11	1.57	1.51	1.51	0.52	1.24
k_3	0.63	0.32	0.26	0.24	0.33	0.21
k_4	0.077	0.13	0.067	0.18	0.073	0.15
k_5	0.61	0.13	1.51	0.78	0.36	0.38
k_6	2.54	3.89	3.56	3.64	1.11	2.94
$k_{\text{total } N_2 \text{ removal}}$	0.30	0.57	0.20	0.41	0.19	0.60

Operating conditions: All catalysts were presulfided at 325°C in 10% H_2S/H_2 for 2 hrs, T = 342°C, P = 34 atm.

A: without CS_2 ; B: with 0.05 wt % of CS_2 in white oil to give gas phase H_2S .

The differences between Co-Mo/ Al_2O_3 and Ni-Mo/ Al_2O_3 increase with severity of operating conditions as shown in Table IV. Under the more severe operating conditions Ni-Mo/ Al_2O_3 is superior by a factor of about 2 for total nitrogen removal rate. The hydrogenation rates (k_1 , k_2 , k_3 and k_5) are all significantly higher over the Ni-Mo/ Al_2O_3 than over Co-Mo/ Al_2O_3 . The behavior for nitrogen-carbon bond rupture is consistent with the relative behavior observed for the less severe conditions.

TABLE IV

CATALYTIC HYDRODENITROGENATION OF QUINOLINE AT MORE SEVERE CONDITIONS

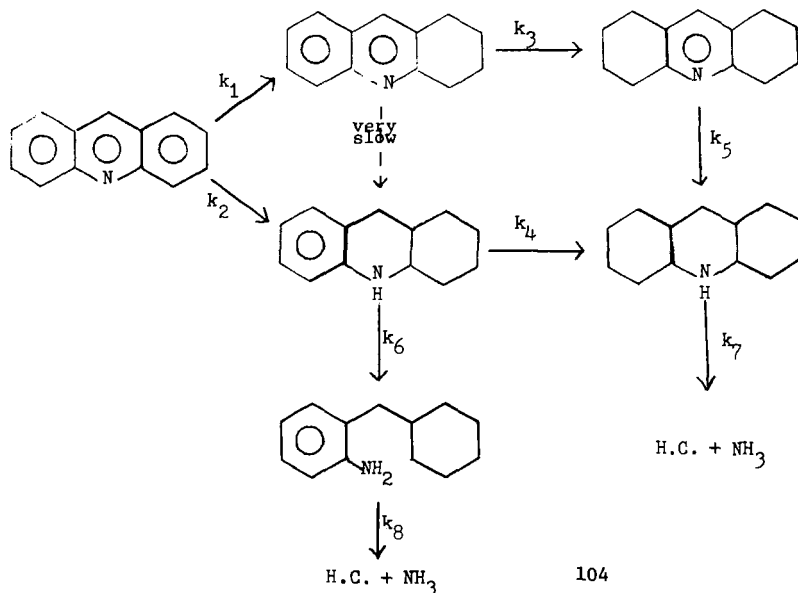
Rate constant, min^{-1}	Ni-Mo/Al ₂ O ₃ (Cyanamid HDS-9A)		Co-Mo/Al ₂ O ₃ (Cyanamid HDS-16A)	
	<u>mild*</u>	<u>severe**</u>	<u>mild*</u>	<u>severe**</u>
k_1	3.09	4.95	1.51	0.69
k_2	1.57	10.55	1.51	2.95
k_3	0.32	4.67	0.24	2.28
k_4	0.13	0.50	0.18	0.51
k_5	0.13	3.40	0.78	1.91
k_6	3.89	10.58	3.64	3.45
$k_{\text{total N-removal}}$	0.57	2.42	0.41	1.22

All catalysts presulfided at 325°C in 10% H₂S/H₂ for 2 hrs, 0.05 wt % CS₂ was added to all runs.

*mild operating conditions: temp., 342°C; total pressure, 34 atm.

**severe operating conditions: temp, 367°C; total pressure, 136 atm.

For acridine the hydrodenitrogenation reaction involves the following reaction network (12):



The effect of different catalysts on the hydrodenitrogenation of acridine is shown in Table V. Hydrogenation rates (k_1 , k_2 , k_3 , k_4 and k_5) are typically more rapid over the Ni-Mo/Al₂O₃ and Ni-W/Al₂O₃ catalysts than over the Co-Mo/Al₂O₃; the Ni-Mo/Al₂O₃ catalysts has a slight advantage over Ni-W/Al₂O₃. The Ni-Mo/Al₂O₃ catalyst shows distinctly higher activity for the carbon-nitrogen bond rupture steps and thus is overall the superior of the catalysts used in these studies.

TABLE V
EFFECT OF CATALYST TYPE ON THE HYDRODENITROGENATION OF ACRIDINE

Rate constant, min ⁻¹	Ni-Mo/Al ₂ O ₃ (Cyanamid HDS-9A)	Co-Mo/Al ₂ O ₃ (Cyanamid HDS-16A)	Ni-W/Al ₂ O ₃ (Nalco NT-550)
k_1	5.0	3.1	7.7
k_2	36.2	19.0	43.0
k_3	7.2	3.67	4.0
k_5	0.38	0.015	0.15
k_4	8.8	2.91	3.77
k_6	1.14	0.43	0.41
k_8	2.20	0.79	0.77
k_7	2.19	0.73	0.76
$k_{\text{total N-removal}}$	1.25	0.48	0.54

Operating conditions: T = 367°C; P = 136 atm; All catalysts presulfided at 425°C for 2 hr in 10% H₂S in H₂; 0.05 wt % of CS₂ in white oil was used in all runs.

Because of the complexity of the hydrodenitrogenation reaction network, involving hydrogenation and carbon-nitrogen bond rupture as distinct reaction steps, the evaluation and further development of hydrodenitrogenation catalysts can be greatly aided by knowledge of the rate of the various intermediate reaction steps in the reaction network. This work shows that Ni-Mo/Al₂O₃ is typically better for hydrodenitrogenation because it has higher hydrogenation activity than Co-Mo/Al₂O₃; Ni-W/Al₂O₃ appears to be slightly less active than Ni-Mo/Al₂O₃. The cracking activities appear to be more dependent on the source of the support and are also very important in determining the relative ranking of overall catalyst behavior. This aspect of catalyst behavior was not sufficiently investigated in this work to allow for firm conclusions.

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STERIC EFFECTS IN PHENANTHRENE AND PYRENE
HYDROGENATION CATALYZED BY SULFIDED Ni-W/Al₂O₃

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The increased interest in coal liquefaction and catalytic upgrading of coal-derived liquids has recently led to a considerable amount of work on hydrodesulfurization and hydrodenitrogenation of model heterocyclic compounds in the presence of sulfided catalyst systems(1,2). In contrast, hydrogenation reactions of model polycyclic aromatic hydrocarbons in the presence of such catalysts have been studied to a limited extent (3-5). It is also noteworthy that in comparison with previous extensive studies on mechanistic and stereochemical aspects of metal-catalyzed hydrogenation of condensed aromatics, so far little attention has been paid to such aspects in hydrogenation studies with the structurally different class of sulfided catalysts.

In the present work the hydrogenation of phenanthrene (1) and pyrene (9) was systematically investigated as a function of sulfided catalyst type, reaction temperature, hydrogen pressure, and catalyst/feed ratio. Experiments were performed in a semi-batch reactor, and products obtained were identified and quantitatively analyzed by a combination of gas chromatography, PMR, and mass-spectral methods (see Experimental).

RESULTS AND DISCUSSION

Relative catalytic activities of sulfided Ni-Mo/Al₂O₃ (catalyst A), Ni-W/Al₂O₃ (catalyst B) and Co-Mo/Al₂O₃ (catalyst C) for hydrogenation of 1 were examined by comparative experiments under mild experimental conditions, i.e. pressure, 1500 psig; temperature, 341°C; reaction time, 2 hr. Under such conditions conversion of 1 into perhydrophenanthrene (8) is incomplete and the product contains, in addition to 8, a series of partially hydrogenated compounds expected from stepwise hydrogenation of phenanthrene (P), i.e. 9,10-dihydroP(2), 1,2,3,4-tetrahydroP(3), 1,2,3,4,9,10,11,12-octahydroP(4), 1,2,3,4,5,6,7,8-octahydroP(5), and isomeric mixtures of decahydroP(6) and dodecahydroP(7). With samples of the above indicated types of catalysts, having comparable concentrations of the active components and nearly identical surface areas and pore volumes, it was found that the decrease in H-aromaticity is 20-25% higher with A and B, as compared with C. Further, under conditions leading to complete saturation of 1 (2,900 psig; 341°C; 7 hr) the hydrogenation selectivity of B was found to be somewhat higher than that of A. Consequently, a catalyst of type B (containing 5.1% of NiO and 20.2% of WO₃; see Experimental) was selected for the hydrogenation study.

Figures 1 and 2 summarize the observed change in product composition from hydrogenation of 1 as a function of temperature in the range of 200-380°C. For the purpose of clarity the composition is plotted in two sets corresponding to anticipated consecutive stages of the hydrogenation process, i.e. an early stage (A) showing the change in concentration of phenanthrene derivatives with one or two hydrogenated rings (Fig. 1), and a later stage showing the change in concentration of derivatives with two or three hydrogenated rings (Fig. 2). Extrapolation of the curves in Fig. 1 to temperatures below 200°C, clearly indicates that 1,2,3,4-tetrahydroP(3) is the main primary product, while the other possible primary product, i.e., 9,10-dihydroP(2), is formed in considerably lower yield. The gradual decrease in the concentration of compound 3 with increase in temperature (Fig. 1) is accompanied by a corresponding increase in the yield of 1,2,3,4,5,6,7,8-octahydroP(5), a product which should be formed by hydrogenation of the residual aromatic end ring in 3. On the other hand, the gradual disappearance of 9,10-dihydroP(2) with temperature is not accompanied by

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any significant formation of the expected second-step hydrogenation product from 2, i.e., 1,2,3,4,9,10,11,12-octahydroP(4). Since conversion of 2 into 3 is a slow, indirect reaction (*vide infra*), these results indicate that 2 is not an important intermediate in the overall hydrogenation process leading to perhydrophenanthrene (8). After reaching a maximum of ~60% b.wt. near 300°C, the concentration of 1,2,3,4,5,6,7,8-octahydroP(5) decreases with further increase in temperature. Figure 2 indicates that hydrogenation of the residual inner aromatic ring in 5, leading to the final product 8, involves the formation of olefinic intermediates, i.e. isomeric mixtures of decahydroP(6) and of dodecahydroP(7). Patterns similar to those indicated in Figs. 1 and 2 are also observed in the study of product composition as a function of hydrogen pressure (between 500-2,900 psig), and of catalyst/phenanthrene ratio.

The results obtained can be rationalized by considering, among other factors, the stereochemistry of the intermediate compounds formed in the stepwise hydrogenation of 1 to 8:

Initiation of the process by hydrogenation of the inner ring in 1 at the 9,10-position produces a somewhat strained hydroaromatic ring. In forming this ring the two aromatic end rings are forced out of coplanarity, and the resulting 9,10-dihydroP(2) shows strong dehydrogenation tendency at temperatures $\geq 250^\circ\text{C}$ (*vide infra*). In contrast, hydrogenation of an end ring in 1, to yield 3, involves formation of a strainless hydroaromatic ring. Fast consecutive hydrogenation of the two end rings in 1 should produce 1,2,3,4,5,6,7,8-octahydroP(5), which is indeed observed as the main intermediate in the process. Examination of steric models of 5 indicates that flatwise adsorption of the residual inner aromatic ring B on the catalyst surface would be difficult as a result of steric interference by the two flexible hydroaromatic rings A and C (Fig. 3). The lower rate of hydrogenating the inner ring as compared to the end rings in 1 is reflected in the accumulation of compound 5 in reaction products formed under mild experimental conditions. Slow hydrogenation of B, however, may proceed by a stepwise doublet mechanism, involving slantwise or edgewise adsorption of 5 by means of the sterically unobstructed 9,10-position. Such mechanism would require formation of olefinic intermediates, e.g. 6 and 7, which are indeed found in the reaction products (Fig. 2).

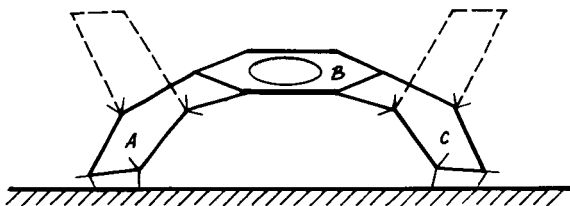


Fig. 3. Steric interference with flatwise adsorption of 1,2,3,4,5,6,7,8-octahydroP(5)

It should be noted that, depending on the surface structure and the strength of adsorption, steric interference of the type indicated in Fig. 3 may not necessarily be equally effective with different types of hydrogenation catalysts. For instance, hydrogenation of 1 using platinum group metals proceeds with strong preference (selectivity $\geq 75\%$) for formation of the *cis-syn-cis*-perhydrophenanthrene stereoisomer (6). This would require (a) preferential flatwise orientation of ring B on the surface; and (b) fast addition of hydrogen from the underside of the adsorbed system, so that all of the four hydrogen atoms found at the asymmetric bridge positions

appear on the same side of the produced hydroaromatic ring. No such selectivity is observed in the present study, viz. the perhydrophenanthrene fraction produced in the presence of sulfided Ni-W/Al₂O₃ consists of a mixture of all six possible stereoisomers in maximal concentrations below 50% of the total fraction. This is in good agreement with the above proposal that in the presence of sulfided catalysts ring B is hydrogenated by a stepwise mechanism, which excludes any possibility of attaining *cis-syn-cis* stereoselectivity.

To confirm the proposed role of 1,2,3,4-tetrahydroP(3) rather than 9,10-dihydroP(2) as the main first-step intermediate in the process, comparative hydrogenation experiments using these two compounds as feeds were carried out under the following conditions: temperature, 250°C; hydrogen pressure, 1500 psig; and reaction time, 3 hr. It is found that 2 yields considerable amounts (17.2% b.wt.) of phenanthrene, which is then converted to perhydroP(8) via the usual intermediates, e.g. compounds 3 and 5. Significantly, the overall rate of conversion of 2 into 8 is lower compared to that observed in the conversion of phenanthrene into 8 under the same set of conditions. In contrast, 1,2,3,4-tetrahydroP(3) does not undergo any dehydrogenation to phenanthrene under identical conditions, and its relative rate of hydrogenation into 8 is markedly higher than that of phenanthrene proper.

The hydrogenation of pyrene(9) in the presence of sulfided Ni-W/Al₂O₃ was investigated as a function of experimental variables, using an analogous procedure. Figures 4 and 5 summarize the change in product composition from 9 (at 341°C) as a function of hydrogen pressure in the range of 1,000-2,900 psig. As seen, only one type of product containing one hydrogenated ring, i.e. 4,5-dihdropyrene (10), is formed. The yield of this first intermediate decreases with increase in pressure, while that of the preferred second-step hydrogenation intermediate, viz. 1,2,3,3a,4,5-hexahdropyrene (12) passes through a maximum at ~1,500 psig and then gradually decreases at higher pressure (Fig. 4). It is found that the yield of the alternative second-step product, i.e. 4,5,9,10-tetrahydropyrene (11), is very low in the entire pressure range, indicating that this compound is not an important intermediate in the hydrogenation process. The strong preference for hydrogenation of 10 into 12 rather than into 11 apparently depends on a marked difference in the position of the respective aromatic saturation equilibria. Compound 11 contains two rather strained hydroaromatic rings which should be susceptible to easy dehydrogenation, whereas 12 contains two non-strained hydroaromatic rings in a skewed chair conformation which should be more resistant to dehydrogenation. Figure 5 indicates that hydrogenation of 12 to yield perhydropyrene (14) involves the intermediate formation of 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene (13), followed by slow hydrogenation of the residual tetrasubstituted aromatic ring in 13. Examination of molecular models shows that flatwise adsorption of this residual aromatic ring on the catalyst surface would be difficult due to steric interference by the three surrounding hydroaromatic rings.

The observed slow rate of hydrogenating the inner ring in 1,2,3,4,5,6,7,8-octahydrophenanthrene (5), and the apparent slow rate of hydrogenating the residual tetrasubstituted ring in 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene (13), to yield perhydropyrene (14), indicate that sterically blocked aromatic rings in polycyclic aromatic-naphthenic systems could be markedly resistant to hydrogenation in the presence of sulfided catalysts. This could provide a plausible explanation for the observed resistance of coal-derived liquids to complete hydrogenation, even in case the aromatic saturation equilibria are fully displaced in the direction of saturation (1).

EXPERIMENTAL

Apparatus - An autoclave of 300 ml capacity, rated at 4,000 psi (510°C), was adopted for use as a semi-batch reactor. The autoclave was equipped with a magnetic stirrer, a temperature-controlled heater, a pressure gage, and a water cooling system. It was connected to a high pressure hydrogen source through a check valve and a regulator permitting the maintenance of a constant pressure throughout the experiment.

Catalysts - A wide range of supported Ni-Mo, Ni-W, and Co-Mo systems, obtained

commercially or prepared in this Department, were used in a preliminary screening of hydrotreating catalysts. The selected catalyst had a surface area of 225 m²/g, and contained NiO, 5.1; WO₃, 20.2; Fe₂O₃, 0.03; and Al₂O₃, 74.1% b.wt. It was sulfided at 300°C and 250 psig with a mixture of hydrogen and carbon disulfide, using an appropriately designed pressure flow system (1).

Procedure - Highly purified samples (> 99%) of phenanthrene and pyrene were used as starting materials. In each experiment were used 13 g of the aromatic compound and 2.6 g of presulfided catalyst. After flushing, the charged autoclave was quickly brought to the desired temperature and hydrogen pressure, and kept under constant conditions for the selected length of time (2 hr in most experiments). At the end of each run, the reaction mixture was rapidly cooled to room temperature, and after releasing the pressure, dissolved in carbon tetrachloride, filtered to remove the catalyst, and analyzed.

Analysis - Products from the hydrogenation reactions were identified by mass spectrometry, PMR analysis, and measurement of gas chromatographic retention volumes. In most cases structures were confirmed by comparison with pure reference compounds. Quantitative analysis of product components was performed by temperature-programmed (60-270°C; 4°C/min) gas chromatography with a 9' x 1/8" column packed with 6% OV-17 on 100-120 mesh Chromosorb W.

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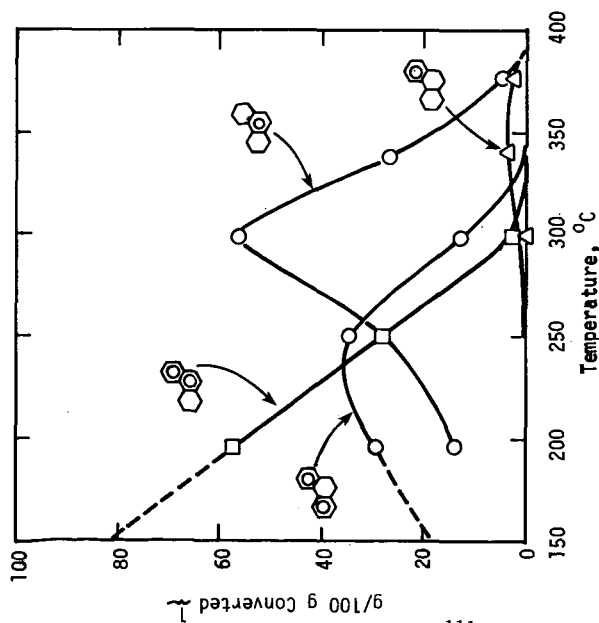


Fig. 1. Change in Product Composition from Hydrogenation of Phenanthrene (Stage A) as a Function of Temperature.

Catalyst: Sulfided Ni-W on Alumina

Pressure: 2900 PSIG

Reaction Time: 2 hr

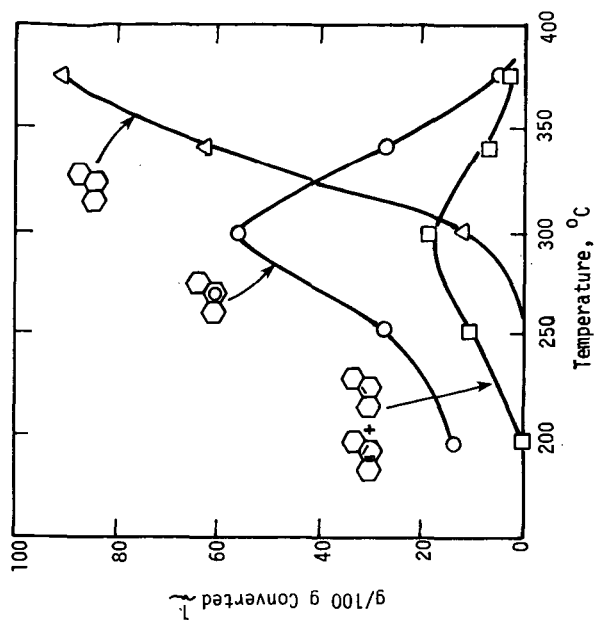


Fig. 2. Change in Product Composition from Hydrogenation of Phenanthrene (Stage B) as a Function of Temperature.

Catalyst: Sulfided Ni-W on Alumina

Pressure: 2900 PSIG

Reaction Time: 2 hr

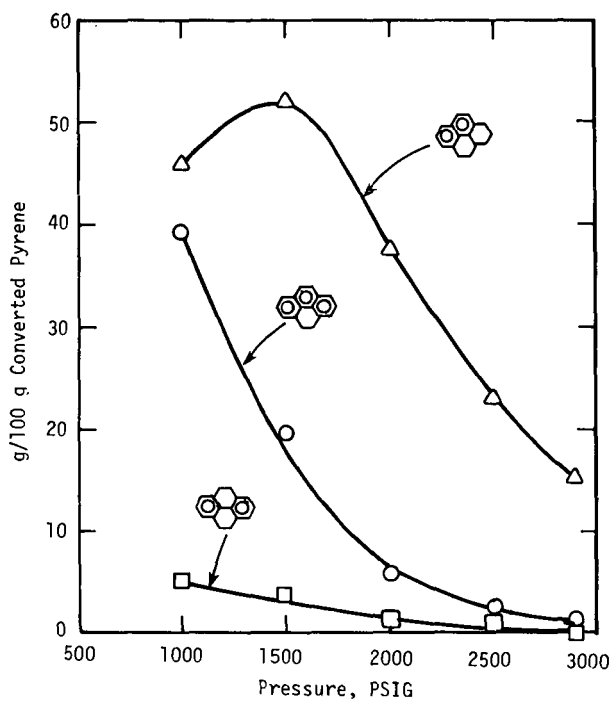


Fig. 4. Change in product composition from hydrogenation of pyrene as a function of pressure (Stage A).

Catalyst: Sulfided Ni-W on Alumina;

Reaction Temperature: 341°C;

Reaction Time: 3 hr.

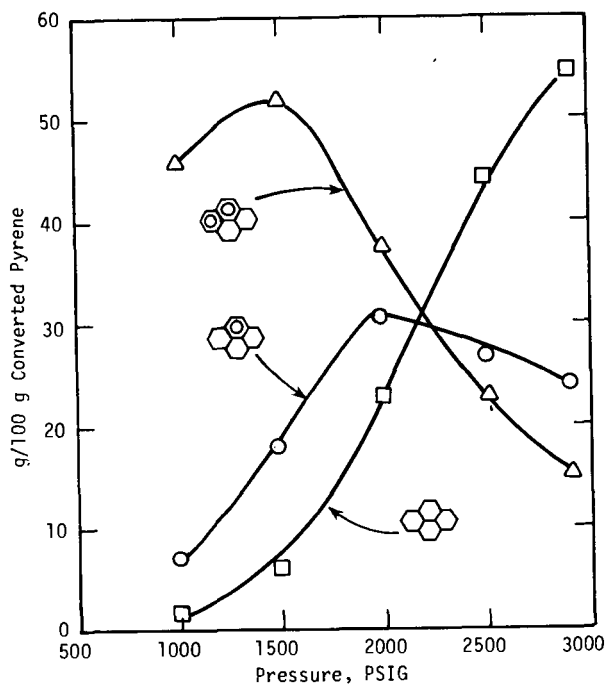


Fig. 5. Change in product composition from hydrogenation of pyrene as a function of pressure (Stage B).
Catalyst: Sulfided Ni-W on Alumina,

Reaction Temperature: 341°C;

Reaction Time: 3 hr.

STERIC EFFECTS IN THE HYDROGENATION-HYDRODENITROGENATION
OF ISOMERIC BENZOQUINOLINES CATALYZED BY SULFIDED

$\text{Ni-W/Al}_2\text{O}_3$

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Mechanistic aspects of sulfide-catalyzed hydrodenitrogenation of N-heterocyclics, and in particular of condensed polycyclic systems, have been studied to a limited extent (1,2). Recently, this subject has attracted more interest and several significant kinetic studies have been reported (3,4). It is noteworthy, however, that so far very little attention has been paid to stereochemical aspects of hydrodenitrogenation processes. In order to obtain a first information on the possible importance of steric effects in such reactions, the hydrogenation-hydrodenitrogenation of two isomeric benzoquinolines, i.e. 5,6-benzoquinoline (1) and 7,8-benzoquinoline (2), was comparatively studied as a function of reaction temperature, hydrogen pressure, and sulfided catalyst type. Experiments were carried out in a semi-batch reactor, and products formed were identified and analyzed by a combination of gas chromatography, PMR, and mass spectrometry.

RESULTS AND DISCUSSION

Figures 1-4 summarize the change in product composition from hydrogenation of the two isomeric benzoquinolines as a function of reaction temperature in the range of 200-380°C, using a sulfided $\text{Ni-W/Al}_2\text{O}_3$ catalyst. As seen from Fig. 1, at temperatures below 250°C, the only product from 2 is 1,2,3,4-tetrahydro-7,8-benzoquinoline (3), derived by selective hydrogenation of the pyridine ring. With increase in temperature above 250°C, there is fast decrease in the yield of this intermediate compound, accompanied by formation of three other derivatives, i.e., 6-propyl-1,2,3,4-tetrahydronaphthalene(4), 2-propylnaphthalene(5), and 1,2,3,4,11,12,13,14-octahydro-7,8-benzoquinoline(6). The presence of compounds 5 and 6 indicates that hydrodenitrogenation of the primary product 3 could occur with or without preliminary hydrogenation of the end benzene ring. It is noted that the yield of 2-propylnaphthalene (5) reaches a maximum at ca 300°C and then decreases with increase in temperature, while the yield of 6-propyl-1,2,3,4-tetrahydronaphthalene(4) continues to increase up to 350°C and only then decreases with further increase in temperature (Fig. 1). This would indicate that 5 plays an important role as a precursor in the formation of 4. The latter could also be derived from 6, but the relatively low yield of this compound indicates that this alternative pathway is of lesser importance. At temperatures between 350-380° (Figure 2) the decrease in the concentration of 4 is accompanied by a corresponding increase in the yield of 2-propyldecalin(7), which is the final product of the hydrodenitrogenation process. At the relatively short contact time of 2 hr, at 341°C, the yield of 2-propyldecalin(7) is only 9%, and 6-propyl-1,2,3,4-tetrahydronaphthalene(4) is the major product (79%). However, at a contact time of 7 hr hydrogenation of 4 into 7 is essentially complete.

Patterns closely similar to those in Figs. 1 and 2 are found in the change of product composition as a function of hydrogen pressure.

Figures 3 and 4 summarize the change in product composition from hydrogenation of 5,6-benzoquinoline(1) as a function of reaction temperature. As seen, at temperatures around 200°C the single product observed is 1,2,3,4-tetrahydro-5,6-benzoquinoline (8), derived by fast, selective hydrogenation of the pyridine ring in 1. The indicated rate of this reaction is higher by at least one order of magnitude than that of the corresponding hydrogenation of 7,8-benzoquinoline(2) to 1,2,3,4-tetrahydro-7,8-benzoquinoline(3). At temperatures > 200°C there is gradual decrease in the

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concentration of 8, accompanied by formation of 1,2,3,4,11,12,13,14-octahydro-5,6-benzoquinoline(9). The yield of this second-step hydrogenation intermediate reaches a maximum around 300°C, and then decreases at higher temperature (Fig. 3). Further, this decrease in the yield of 9 (Fig. 4) is accompanied by a corresponding gradual increase in the yield of the hydrodenitrogenation product, 5-propyl-1,2,3,4-tetrahydronaphthalene(10), indicating that hydrodenitrogenation is mainly accomplished subsequent to the saturation of the end benzene ring. As seen from Fig. 4, at temperatures >300°C the product contains also small amounts (5-8%) of 1-propylnaphthalene (11), indicating that direct hydrodenitrogenation of the primary product 8 occurs to a minor extent. At reaction temperatures of ca 340-380° part of compound 10 is further hydrogenated to give 1-propyldecalin (12) which can be considered as the final product of the hydrodenitrogenation process. If the temperature is kept at ca 340°C and the reaction time is extended, or the pressure increased, compound 10 is converted largely into 12, without any significant extent of cracking. At ca 380°C, however, some cracking of compound 10 occurs to form 1,2,3,4-tetrahydronaphthalene (Fig. 4).

The study of the reaction of 5,6-benzoquinoline(1) as a function of catalyst type indicates that there is no significant difference in the hydrogenation-hydrodenitrogenation activity of sulfided Ni-W/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts.

The observed markedly slower hydrogenation of the pyridine ring in 7,8-benzoquinoline(1) can be ascribed to the steric hindrance effect of the 7,8-benzo group, which prevents edgewise adsorption of the pyridine ring to acidic sites on the catalyst surface by means of the nitrogen electron pair(5). In contrast, hindrance-free adsorption of this type, with consequent strong polarization and activation of the pyridine moiety is easily attained in the case of 5,6-benzoquinoline(1). Following the hydrogenation of the pyridine rings in 1 and 2 to give 1,2,3,4-tetrahydro-5,6-benzoquinoline(8) and 1,2,3,4-tetrahydro-7,8-benzoquinoline(3), respectively, there are marked differences in the subsequent reaction pathways leading to hydrodenitrogenation of these two isomeric intermediates, i.e. compound 3 undergoes direct hydrodenitrogenation to yield 2-propylnaphthalene(5), whereas 8 undergoes essentially complete hydrogenation of the end benzene ring, to form 1,2,3,4,11,12,13,14-octahydro-5,6-benzoquinoline(9), prior to the hydrogenolysis step (*vide supra*). This could be ascribed to differences in the steric characteristics of the intermediates involved. Examination of molecular models shows that in compound 3 the N-atom is in a *peri*-position relative to the aromatic H at C-14. This should cause some displacement of the nitrogen out of coplanarity with the aromatic system, and should facilitate the hydrogenolysis of the C-N bonds, leading to formation of 2-propylnaphthalene(5). In contrast, the 5,6-benzo group in 8 does not interact sterically with the hydrogenated pyridine ring, *viz.* in this case there is no destabilizing effect upon the C-N bonds. Consequently, 8 is hydrogenated to compound 9 prior to the hydrogenolysis step, which produces 5-propyl-1,2,3,4-tetrahydronaphthalene(10).

The results obtained indicate that the rate and depth of hydrodenitrogenation of coal-derived liquids may strongly depend on the steric characteristics of condensed N-heterocyclic-aromatic components, or of partially hydrogenated reaction intermediates formed during the process.

EXPERIMENTAL

The apparatus, as well as the experimental and analytical procedures were essentially the same as used in the preceeding study of phenanthrene and pyrene hydrogenation.

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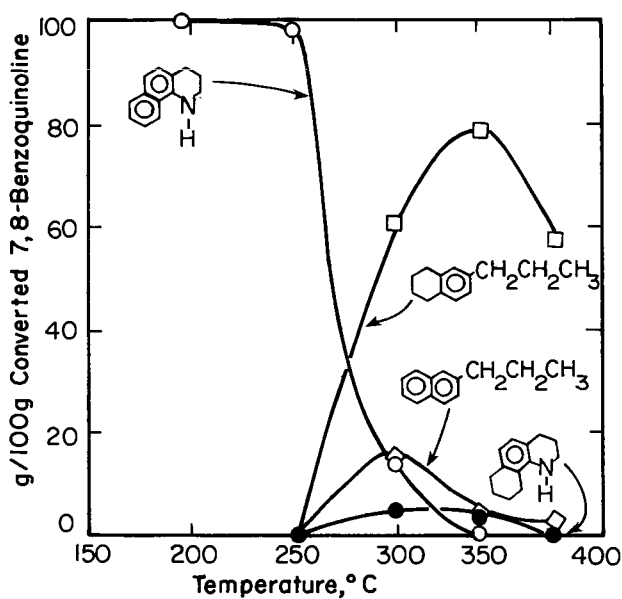


Fig. 1. Change in product composition from hydrodenitrogenation of 7,8-Benzoquinoline as a function of temperature (Stage A).

Catalyst: Sulfided Ni-W/Al₂O₃

Pressure: 2900 psig;

Reaction time: 2 hr.

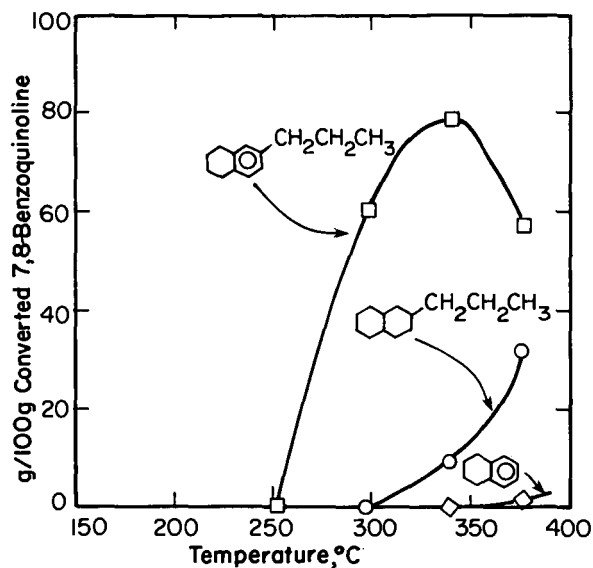


Fig. 2. Change in product composition from hydrodenitrogenation of 7,8-Benzoquinoline as a function of temperature (Stage B).

Catalyst: Sulfided Ni-W/ Al_2O_3

Pressure: 2900 psig;

Reaction time: 2 hr.

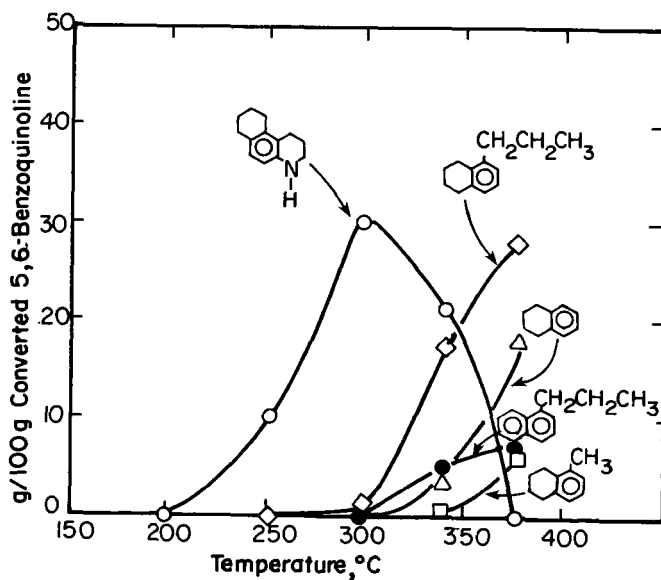


Fig. 4. Change in product composition from hydrodenitrogenation of 5,6-Benzoquinoline as a function of temperature (Stage B).

Catalyst: Sulfided Ni-W/ Al_2O_3

Pressure: 2900 psig;

Reaction Time: 2 hrs.

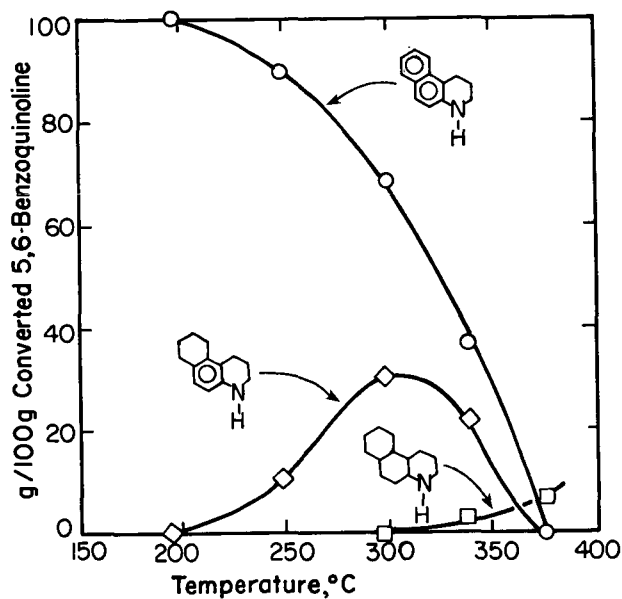


Fig. 3. Change in product composition from hydrodenitrogenation of 5,6-Benzoquinoline as a function of temperature (Stage A).

Catalyst: Sulfided Ni-W/Al₂O₃
 Pressure: 2900 psig;
 Reaction Time: 2 hrs.